IFW

16

Practitioner's Docket No. FINETEX 4.0-001 **PATENT**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Steven H. Bertz, et al.
Application No.: 10 / 617,497 Group No.:
Filed: July 11, 2003 Examiner:
For: COMPOSITIONS CONTAINING PHENETHYL ARYL ESTERS AS SOLUBILIZING AGENTS FOR ACTIVE ORGANIC COMPOUNDS

Assistant Commissioner for Patents
Washington, D.C. 20231

THIRD-PARTY SUBMISSION IN PUBLISHED APPLICATION (37 C.F.R. § 1.99)

NOTE: 37 C.F.R. § 1.99(e): "A submission under this section must be filed within two months from the date of publication of the application (§ 1.215(a)) or prior to the mailing of a notice of allowance (§ 1.311), whichever is earlier. Any submission under this section not filed within this period is permitted only when the patents or publications could not have been submitted to the Office earlier, and must also be accompanied by the processing fee set forth in § 1.17(i). A submission by a member of the public to a pending published application that does not comply with the requirements of this section will be returned or discarded."

NOTE: 37 C.F.R. § 1.99(f): "A member of the public may include a self-addressed postcard with a submission to receive an acknowledgment by the Office that the submission has been received. A member of the public filing a submission under this section will not receive any communications from the Office relating to the submission other than the return of a self-addressed postcard."

NOTE: 37 C.F.R. § 1.99(f): "In the absence of a request by the Office, an applicant has no duty to, and need not, reply to a submission under this section."

1. The above identified application has been published on Jan. 13, 2005 (Date).

WILLIAM R. DIXON, JR.
SPECIAL PROGRAM EXAMINER
4/4/05

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37 C.F.R. § 1.10*

☒ as "Express Mail Post Office to Addressee" Mailing Label No. EV 447666251 (mandatory)

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☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 3-10-05

Edward R. Weingram
Signature

Edward R. Weingram
(type or print name of person certifying)

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- ☐ after two months from the date of publication of the above application and the patents and/ or publications listed below could not have been submitted to the Office earlier.
  - ☐ the processing fee set forth in § 1.17(i) accompanies this submission.

NOTE: 37 C.F.R. § 1.99(b): "A submission under this section must identify the application to which it is directed by application number and include:

(1) The fee set forth in § 1.17(p);

(2) A list of the patents or publications submitted for consideration by the Office, including the date of publication of each patent or publication;

(3) A copy of each listed patent or publication in written form or at least the pertinent portions; and

(4) An English language translation of all the necessary and pertinent parts of any non-English language patent or publication in written form relied upon."

2. Attached hereto is:

NOTE: 37 C.F.R. § 1.99(d): "A submission under this section shall not include any explanation of the patents or publications, or any other information. The Office will dispose of such explanation or information if included in a submission under this section. A submission under this section is also limited to ten total patents or publications."

- ☒ A list of the patents or publications submitted for consideration by the Office, including the date of publication of each patent or publication.
- ☒ A copy of each listed patent or publication in written form
  - ☒ Except that only the pertinent portions of the only of the following listed patents and publications are being provided *See below
- ☐ An English language translation of all the necessary and pertinent parts of any non-English language patent or publication in written form relied upon.

NOTE: 37 C.F.R. § 1.99(f): "No further submission on behalf of the member of the public will be considered, unless such submission raises new issues which could not have been earlier presented."

3. ☐ This submission is in addition to the submission which was made on _____ *(Date)* and is being made because ir raises new issues which could not have been earlier presented.

NOTE: 37 C.F.R. § 1.99(c): "The submission under this section must be served upon the applicant in accordance with § 1.248."

NOTE: 37 C.F.R. § 1.248:

"(a) Service of papers must be on the attorney or agent of the party if there be such or on the party if there is no attorney or agent, and may be made in any of the following ways:

(1) By delivering a copy of the paper to the person served;

(2) By leaving a copy at the usual place of business of the person served with someone in his employment;

(3) When the person served has no usual place of business, by leaving a copy at the persons residence, with some person of suitable age and discretion who resides there;

(4) Transmission by first class mail. When service is by mail the date of mailing will be regarded as the date of service;

(5) Whenever it shall be satisfactorily shown to the Commissioner that none of the above modes of obtaining or serving the paper is practicable, service may be by notice published in the Official Gazette.

*1) U.S. Pat. No. 5,998,120 to Connelly et al. issued 12/07/99 (front page and columns 5&6 only).

2) Excerpt (pages 1&5) from the website of Dermatest GmbH, http://www.dermatest.de/EN/Presentation/body_presentation.html, entitled "Presentation of Dermatest GmbH", download date March 9, 2005.

(b) Papers filed in the Patent and Trademark Office which are required to be served shall contain proof of service. Proof of service may appear on or be affixed to papers filed. Proof of service shall include the date and manner of service. In the case of personal service, proof of service shall also include the name of any person served, certified by the person who made service. Proof of service may be made by:

(1) An acknowledgement of service by or on behalf of the person served or

(2) A statement signed by the attorney or agent containing the information required by this section."

4. Service of this paper and the attachements thereto have been made on the applicant and the proof of such service is attached.

5. Fees Due

☒ Fee set forth in § 1.17(p) ($180.00) $ 180.00

☐ Fee set forth in § 1.17(i) ($130.00) $ _____

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6. Payment of fees

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☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

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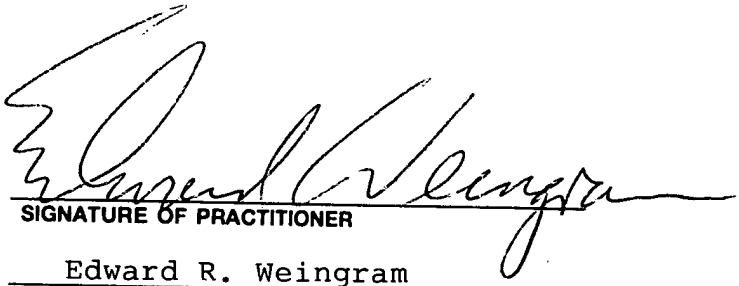

SIGNATURE OF PRACTITIONER

Edward R. Weingram

(type or print name of practitioner)

WEINGRAM & ASSOCIATES, P.C.
P.O. Address P.O. BOX 927
MAYWOOD, N.J. 07607

List of Patents	Date of Publication
1. U.S. Patent No. 4,791,097 to Walele, et al.	Issued December 13, 1988
2. U.S. Patent No. 6,635,775 to Walele, et al.	Issued October 21, 2003
3. U.S. Patent No. 5,998,120 to Connelly et al.	Issued December 7, 1999

List of Publications and Dates of Publication

4. Technical Data Sheet, Solubility of Parsol 1789 in Finsolv TN, Finsolv TPP, Finsolv PG-22 and Finsolv EB, by Finetex, Inc., dated November 1997.

5. Technical Data Sheet, Solubility of Benzophenone-3 in Finsolv TN, Finsolv TPP, Finsolv PG-22 and Finsolv EB, by Finetex, Inc., dated November 1997.

6. Technical Data Sheet for FINSOLV® TPP, INCI Name: C12-15 Alkyl Benzoate (and) Dipropylene Glycol Dibenzoate (and) PPG-15 Stearyl Ether Benzoate, by Finetex, Inc., dated April 2000.

7. Technical Data Sheet for FINSOLV® PG-22, INCI Name: Dipropylene Glycol Dibenzoate, by Finetex, Inc., dated April 2000.

8. Technical Data Sheet for FINSOLV® EB, INCI Name: Ethylhexyl Benzoate, by Finetex, Inc., dated June 21, 2002.

9. Finetex® Cosmetics & Personal Care Products Index, by Finetex, Inc., dated March 2002.

10. Excerpt (pages 1 and 5) from the website of Dermatest GmbH, **http://www.dermatest.de/EN/Presentation**/body_presentation.html, entitled "Presentation of Dermatest GmbH", download date March 9, 2005.

Patent

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Steven H. Bertz, et al.

Serial No.: 10/617,497

Filed: July 11, 2003

For: Compositions Containing Phenethyl Aryl Esters As Solubilizing Agents For Active Organic Compounds

Examiner: Hector M. Reyes
Group Art Unit: 1625

CERTIFICATE OF SERVICE

I hereby certify that a copy of the foregoing Third-Party Submission in Published Application, including ten references, was served on applicants through their intellectual property counsel, in compliance with 37 CFR 1.248(b), by first class mail, postage prepaid to:

William J. Davis, Esq.
International Specialty Products
Legal Dept., Bldg No. 10
1361 Alps Road
Wayne, NJ 07470

on this 10th day of March, 2005.

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Maywood, NJ 07607
Tel: (201) 843-6300
Fax: (201) 843-6495

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

EV 447666251

RE: Our File: FINETEX 4.0-001 Serial Patent (APPLN.) No.: 10/617,497

Applicant: BERTZ, et al. Group Art Unit:

Filed: 07/11/03 Examiner:

For: COMPOSITIONS CONTAINING ARYL ESTERS AS SOLUBILIZING AGENTS FOR ACTIVE ORGANIC COMPOUNDS Batch No.:

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( )	Letter-Official Draftsman	( )	Affidavit/Declaration
( )	Preliminary Amendment	( )	Petition
( )	Notice of Appeal/Motion/Brief	( )	Information Disclosure Statement
( )	Assignment/Cover Sheet	( )	Small Entity Statement
( )	TABS _____ to _____	( )	Issue Fee/Maint.Fee
( )	Certificate of Correction	( )	Sworn Translation
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	Drawings ___ sheets - Formal/Informal	(X)	PROOF OF SERVICE ON APPLICANT'S COUNSEL
(X)	3RD PARTY SUBMISSION IN PUB. APPLN	(X)	LIST OF PATENTS/PUBS AND
(X)	10 PUB/PUBLICATIONS	( )	DATES OF PUBLICATION

Conditional Petition and Fee for Extension of Time: If any extension of time for the accompanying response is required, applicant requests that this be considered a petition therefor.

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SIGNED: Edward R. Weingram

DATED: 3-10-05

Respectfully submitted,

Edward R. Weingram
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WEINGRAM & ASSOCIATES, P.C.
P.O. Box 927
Maywood, NJ 07607

TEL: (201) 843-6300
FAX: (201) 843-6495

Enclosures
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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

RE: Our File: FINETEX 4.0-007

Applicant: BERTZ, et al.

Filed: 07/11/03

For: COMPOSITIONS CONTAINING ARYL ESTERS AS SOLUBILIZING AGENTS FOR ACTIVE ORGANIC COMPOUNDS

Serial Patent (APPLN.) No.: 10/617,497

Group Art Unit:

Examiner:

Batch No.:

Enclosed for filing in the U.S. Patent and Trademark Office are:

( ) Utility/Design/Provisional/Patent Application

(X)	Law Firm Transmittal Letter-copy	( )	Response/Amendment
( )	Letter-Official Draftsman	( )	Affidavit/Declaration
( )	Preliminary Amendment	( )	Petition
( )	Notice of Appeal/Motion/Brief	( )	Information Disclosure Statement
( )	Assignment/Cover Sheet	( )	Small Entity Statement
( )	TABS _____ to _____	( )	Issue Fee/Maint.Fee
( )	Certificate of Correction	( )	Sworn Translation
(X)	Check No. 7205 - $ 180-	(X)	Postcard acknowledging receipt of the above identified material
	Drawings ___ sheets - Formal/Informal	(X)	PROOF OF SERVICE ON APPLICANT'S COUNSEL
(X)	3RD PARTY SUBMISSION IN PUB. APPLN	(X)	LIST OF PATENTS/PUBS AND
(X)	10 PUB/PUBLICATIONS	( )	DATES OF PUBLICATION

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In connection with the above-identified matter, please charge any additional fees or any other charges related to this matter to the deposit account of the writer, No. 23-0812. A duplicate copy of this letter is enclosed.

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AND IS ADDRESSED TO THE COMMISSIONER FOR PATENTS, P.O.Box 1450, Alexandria, VA 22313-1450

SIGNED: Edward R. Weingram

DATED: 3-10-05

Respectfully submitted,

Edward R. Weingram

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TEL: (201) 843-6300
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Enclosures
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EXHIBIT - 1

United States Patent [19]

Walele et al.

[11] **Patent Number: 4,791,097**

[45] **Date of Patent: Dec. 13, 1988**

[54] BENZOIC ACID ESTERS AND THEIR USE

[75] Inventors: **Ismail Walele**, Saddle Brook; **Herman Brown**, Teaneck; **Michael Esposito**, Randolph, all of N.J.

[73] Assignee: **Finetex, Inc.**, Elmwood Park, N.J.

[21] Appl. No.: **23,767**

[22] Filed: **Mar. 9, 1987**

[51] **Int. Cl.**[4] **C07C 9/76; C09B 3/22**

[52] **U.S. Cl.** **560/112**; 252/358; 560/103

[58] **Field of Search** 560/103, 112; 252/358

[56] **References Cited**

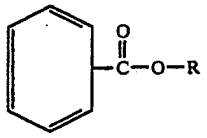
U.S. PATENT DOCUMENTS

2,840,594	1/1958	Coates	560/112
4,323,693	4/1982	Scala	560/103
4,323,694	4/1982	Scala	560/103
4,365,084	12/1982	Young	560/103
4,431,837	2/1984	Geria	560/112
4,559,226	12/1985	Fogil	560/103

Primary Examiner—Paul J. Killos
Attorney, Agent, or Firm—Weingram & Zall

[57] **ABSTRACT**

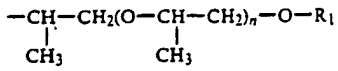
A method is provided for modifying foam in an aqueous surfactant composition. The method comprises admixing with the aqueous surfactant composition a foam modifying amount of a composition of the formula:



wherein R is:

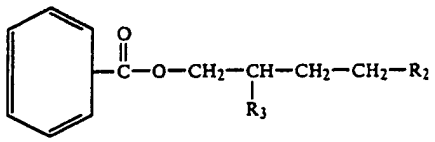
(a) a branched or linear alkyl of 20 to 28 carbon atoms; or

(b)



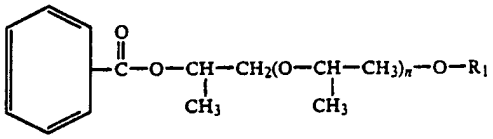
wherein n is 9–16 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms.

Certain of these benzoate esters are novel, in particular:



wherein R_2 and R_3 are each, independently, an alkyl of 4 to 16 carbon atoms, and the total number of carbon atoms in R_2 and R_3 is at least 12 carbon atoms. Preferably, R_2 and R_3 are each C_8H_{17}, i.e. octyldodecyl benzoate ester.

Additional novel benzoate esters used as foam enhancers have the formula:



wherein n is 12 to 16 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms. Particularly preferred esters are when n is 14, R_1 is $C_{18}H_{37}$ and R_1 is C_4H_9. Also, additionally, preferred esters are where n is 9 and R_1 is $C_{16}H_{33}$.

10 Claims, No Drawings

BENZOIC ACID ESTERS AND THEIR USE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to improved ester compositions, and more particularly to certain benzoic acid esters of alcohols which are useful as foam modifiers as well as diluents, solvents, plasticizers, liquid carriers, emollients, conditioners.

2. Description of the Prior Art

There are numerous references which describe the production and use of benzoic acid esters. None of these references teach or suggest the specific novel benzoate esters of this invention or the use of these and other benzoate esters as foam modifiers in detergent compositions. More specifically:

U.S. Pat. No. 2,088,085 to Gross describes a composition added to solutions to produce a stable foam, especially for fire extinguishing purposes. The compound is an ether which the formula R_1—(O—CH_2—CH_2-)$_n$—O—R_2 where R_1 is a hydrogen atom or an alkyl radical and R_2 may be an alkyaryl or aryl radical, n may be a whole number and the total number of carbon atoms is at least three.

U.S. Pat. No. 3,510,500 to Walsh describes a process for preparing an ester by reacting a monobasic organic acid, which may be a benzoic acid, with an organic halide. This reaction requires the removal of hazardous hydrogen halide gas as a byproduct.

U.S. Pat. No. 3,714,228 to Massie describes the production of an ester by reacting a carboxylic acid with an alcohol. An example of a carboxylic acid mentioned therein is benzoic acid and an example of an alcohol is eicosene alcohols (C_{20} alcohols).

U.S. Pat. No. 3,799,969 to Hoppe describes the production of o-aminobenzoic acid-2-hexyldecyl-(1)-ester by the reaction of o-aminobenzoic acid and 2-hexyldecanol.

French Pat. No. 2,151,503 to Beiersdorf Ag. describes $H_2NC_6H_4CO_2CH_2CHRR_1$ as an intermediate, where R is H, C2-12 alkyl and R_1 is OBu, C_{4-14} alkyl.

European patent application No. 0 037 542 (corresponding to U.S. Pat. No. 4,339,342 to Hempel) describes the use of 2-octyldodecanol or a mixture of C_{22-30} Guerbet alcohols and hydrophobic, colloidal silicic acid reacted to prepare an anti-foaming agent. This foam inhibition "is surprising in view of known foaming bath additives, such as, for example, those disclosed in German published application (DOS) No. 19 48 500, which contain from 5 to 50 percent of the Guerbet alcohol 2-octyldodecanol" (U.S. Pat. No. 4,339,342, Col. 2 lines 50–58). Although octyldodecanol is cited as a known "foaming bath additive", our work shows that benzoate esters from octyldodecanol are superior foam stabilizers/enhancers/modifiers when compared to octyldodecanol. This is unexpected in that one skilled in the art would assume that the ester would be a foam suppressor when compared to the reactant alcohol. Further, Hempel only teaches the use of octyldodecanol as a carrier or vehicle for foam inhibiting formulations and not as a reactant. Applicants herein only use octyldodecanol as a reactant.

The assignee herein, Finetex Incorporated, has published and patented inventions related to this art, in particular:

Cosmetics and Toiletries, "A new cosmetic fluid emollient for use in antiperspirants", 1980, 95(7), 51–4 by H. Brown describes the use of a C_{12-15} benzoate ester fluid emollients (FINSOLV TN) in antiperspirant preparations.

U.S. Pat. No. 4,278,655 to Elmi describes the use of benzoic acid esters of a mixture of linear primary alcohols in the C_9 to C_{15} carbon chain length range in antiperspirant compositions.

U.S. Pat. No. 4,275,222 to Scala, Jr., describes the benzoic acid esters of a mixture of C12, C13, C14 and C15 linear primary alcohols. The compositions described therein are said to have anti-foaming properties, i.e. they prevent foam from forming initially, and are used in hand cleaners, dispersable bath oils, and floating bath oils.

U.S. Pat. No. 4,293,544 to Elmi describes the use of benzoic acid esters of a mixture of C12, C13, C14 and C15 linear primary alcohols in toiletries, cosmetics, topical pharmaceuticals and the like.

U.S. Pat. No. 4,322,545 to Scala, Jr. describes benzoic acid esters wherein the alcohol is from C12 to C15 primary alcohols. The compositions described therein are said to lack greasiness, oilness, have a low cloud point and pour point, bland odor, ability to form gels with suspending agents and low toxicity.

U.S. Pat. No. 4,323,693 to Scala, Jr. describes a substantially pure benzoic acid ester of isostearyl (C_{18}) alcohol for use as a carrier or vehicle, emollient or solublizer for cosmetic and toiletry formulations.

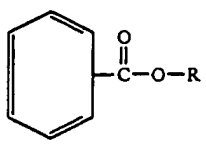
U.S. Pat. No. 4,323,694 to Scala, Jr. describes benzoic acid esters of alcohols which are branched primary alcohols up to C_{18} and branched or linear alcohols up to C_{19}. The esters are used in bubble bath oils and do not significantly alter the foaming properties of the detergents (Col. 14, lines 21-26). When used in a toilet soap bar, "the user should readily observe a richer and denser lather compared to what he or she was used to from regular soap".

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of this invention to provide a method of modifying, while not suppressing, foam in an aqueous surfactant composition using certain specific types of benzoic acid esters.

It is a further object of this invention to provide novel benzoic acid esters which may serve as emollients, solubilizers and carriers (dilutents) and which may also modify the foam and foaming characteristics, without significantly suppressing the foam or foaming characteristics, of the unmodified aqueous surfactant composition.

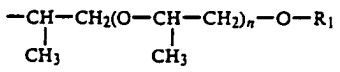
A method is provided for modifying foam and foaming characteristics of an aqueous surfactant composition. The method comprises admixing with the aqueous surfactant composition a foam modifying amount of a composition of the formula:



wherein R is:

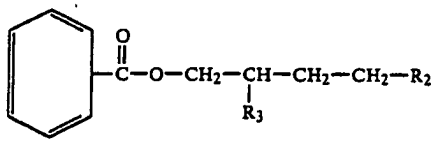
(a) a branched alkyl of 20 to 28 carbon atoms; or

(b)



wherein n is 9–16 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms.

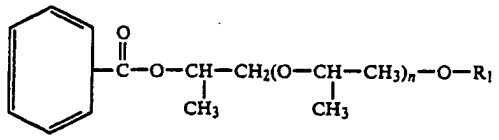
Certain of these benzoate esters are novel, in particular:



wherein R_2 and R_3 are each, independently, an alkyl of 4 to 16 carbon atoms, and the total number of carbon atoms in R_2 and R_3 is at least 12 carbon atoms.

Preferably, R_2 and R_3 are each C_8H_{17}, i.e. octyldodecyl benzoate ester.

Additional novel benzoate esters used as foam modifiers have the formula:



wherein n is 1 to 50 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms. Particularly preferred esters are when n is 14, R_1 is $C_{18}H_{37}$ and R_1 is C_4H_9. Additionally preferred esters are when n is 9 and R_1 is $C_{16}H_{33}$.

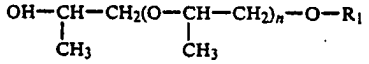
DETAILED DESCRIPTION OF THE INVENTION

The benzoic acid esters of this invention are produced by reacting benzoic acid with an alcohol. Preferably, stannous oxalate is used as a catalyst. It is contemplated, however, that any method of producing such benzoic acid esters can be utilized as long as such method does not interfere with their intended use. In particular, the process for producing the esters should permit them to be purified to a substantially pure condition. By the use of the term "substantially pure", it is meant that the compositions do not contain impurities which would interfere with their intended use, e.g. as foam modifiers in aqueous surfactant compositions.

The alcohol precursors used in preparing the benzoic acid esters are selected from the group consisting of:

(a) branched or linear alkanols of 20 to 28 carbon atoms; or

(b)



wherein n is 1 to 50 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms.

Particularly preferred alcohols are octyldodecanol, propoxylated stearyl alcohol i-e PPG-15 stearyl ether, arachidyl alcohol, behenyl alcohol, and alkanols of 20 to 28 carbon atoms in length, as exemplified by EPAL 20+ alcohol from Ethyl Corporation. The following is a list of alcohols which may be reacted with benzoic acid to produce the novel esters of this invention and the esters used in this invention:

(a) branched or linear alkanols of 20 to 28 carbon atoms:

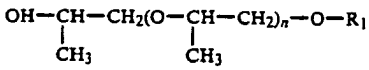
octyldodecanol

arachidyl alcohol

behenyl alcohol

C_{20}+ linear alcohols (Epal 20+)

(b)



wherein n is 1 to 50 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms:

Procetyl-10 (PPG-10 Cetyl Ether) from Croda Inc.

Arlamol E (PPG-15 Stearyl Ether) from I.C.I.

Generally propoxylated alkanols, linear or branched.

The aforedescribed alcohols are well known and commercially available.

The compositions of this invention are useful as foam modifiers for aqueous surfactant compositions. Aqueous surfactant compositions which can utilize such foam modifiers are:

hand clearners

bath compositions

facial cleansers

cleansing creams

hard surface cleaners

shampoos

'mousse' products

shaving creams

pet cleaners

concrete air-entrainment products

ore beneficiation products

The foregoing list is only exemplary of the type of compositions in which the benzoic acid esters may be used and, as such, is not to be considered limiting.

The amount of ester used in the aqueous surfactant composition is dependent on the type of composition desired, the type and quantity of other ingredients used, e.g. cosmetic ingredients, and the amount and type of functional additives that are utilized. Typically, the amount ranges from about 0.5% to about 50% by weight of the aqueous surfactant composition. Preferably, from about 0.5% to about 5.0% of benzoic acid esters of this invention are used.

The afore-described benzoic acid esters have unique properties. In particular, they have foam modifying properties. By "foam modification" herein it is meant that the benzoic acid esters confer any or all of the following properties upon a surfactant composition:

Flash foam increase

Foam volume increase

Foam viscosity increase or decrease

Foam cell size increase or decrease.

While the particular foam modification is dependent upon the benzoic acid ester and surfactant of choice, no surfactant investigated has been observed to suffer a suppression of foam volume due to the presence of any of the benzoic acid esters investigated herein, i.e. none of the benzoic acid esters investigated were defoamers. Additionally, they have other properties which make them suitable for use as emollient carriers in cosmetic formulations, and for use as solvents and emollient car-

riers in general cleaning compositions. Further, they possess other unusual physico-chemical properties, in particular high spreading coefficients, which can make them beneficial and unique components of sophisticated delivery systems—such as in hand, face, and body creams and lotions.

The afore-described benzoic acid esters have the following properties:

1. Lack of greasiness, pleasant skin feel.
2. Lack of oiliness while imparting good lubrication.
3. Low cloud points and pour points.
4. Low toxicity.
5. Ease of emulsification.
6. Unusually high spreading coefficient.
7. Acid, alkaline stability.
8. Solvents for many common skin and hair care additives, including, sunscreens and over-the-counter therapy 'actives'.

The following are non-limiting examples of the compositions of this invention and the uses of these compositions in hair and skin care compositions wherein foam modification and properties related to application and delivery are useful.

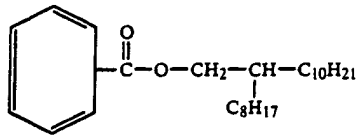
Skin Lotion (Sunscreen)	Wt %	Shampoo	Wt %	"Creamy" Soap Bar	Wt %
Water	82.0	Triethanol-amine Lauryl Sulfate	12.0	"Soap Chips"*	98.0
Glycerin	3.0	Lauramide DEA	3.0	Stearoxy PPG-15-Benzoate	2.0
Cetyl Alcohol	2.0	Octyldodecyl Benzoate	5.0	Color, fragrance	q.s
Stearoxy PPG-15-Benzoate	5.0	Ethylene Glycol Monostearate	1.0		
Tween 80	4.0	Water	79.0		
Ethylene Glycol Monostearate	1.0	Color, fragrance	q.s		
Escalol 507	3.0				

*@ approx 10% water.

EXAMPLE 1

Preparation of Octyldodecyl Benzoate

A mixture of 213 gms. (0.715 moles) of STANDAMUL G from Henkel Co. (Octyldodecanol) and 15 mgms. Sodium borohydride was stirred at room temperature 25° C. under nitrogen. The mixture was then heated and brought to 60° C. and held at 60° C. for ½ hour. To this mixture was added 86.40 gms. (0.68 moles) Benzoic Acid and 450 mgms. of stannous oxalate. The reaction mixture was then further heated to 255° C. During the heat-up cycle, distillate was collected, particularly when the reaction mixture reached a temperature of 170° C. and higher. The reaction was rapidly heated from 60° C. to 177° C. over 45 minutes, and then from 177° C. to 228° C. over the next 60 minutes while still collecting the distillate. Further heating was continued to bring the temperature to 255° C. over the next 30 minutes. The distillate collected contained 7.5 gms. of water and also contained some benzoic acid trapped during the collection of distillate. The reaction was then cooled. The yield at this stage was 265 gm. and acidity was at 9.5 mgms. The KOH/gm. hydroxyl value of this mixture was 19.29. 220 gms. of this ester was treated with 2.2 gms. sodium carbonate, 1.1 gm. sodium chloride, 2.0 gms. Hydrogen peroxide in 35 gms. deionized water. The mixture was stirred and heated to 85°-90° C., held at 85°-90° C. for 30 minutes and allowed to stand for separation of the ester and water phases. The ester phase was separated and further washed with deionized water until reaction of the water was neutral. The ester collected was 200 gms. and was hydrous. The product was vacuum stripped to remove the residual moisture, and then filtered using filter-aids. The final product was a clear liquid and had the following formula:



The following typical physical and chemical properties were observed:

Specific Gravity @ 29° C.:	0.90
Surface Tension @ 25° C.:	32.6 dynes/cm
Spreading Coefficient @ 25° C.:	32.1 dynes/cm
Pour Point:	<−18° C.
Odor:	Bland
Toxicity: Practically non-irritating (eyes), Primary Skin Irritation Score 0.7,	LD_5>5.0 g/kg
Appearance:	Clear liquid
Viscosity @ 25° C. (Brookfield #1, 50 rpm):	45 cps

EXAMPLE 2

Preparation of Octyldodecyl Benzoate

A mixture of 710 gms. (2.38 moles) of Octyldodecanol (STANDAMUL G from Henkel Co.) and 50 mgms. Sodium borohydride was stirred into nitrogen. The mixture was heated to 60° C. and stirred for 30 minutes. 289 gms. (2.28 moles) of Benzoic Acid and 1.5 gms. of stannous oxalate was added. The reaction mixture was heated from 60° C. to 180° C. over one hour. The reaction was held at 180° C. for 30 minutes, distillate being collected. The mixture was further heated to 210°-220° C. over the next 30 minutes, and then held at 210°-220° C. for 30 minutes. The temperature was then raised to 250° C. and the reaction was then held at 250° C. for two hours. The reaction mixture was cooled under nitrogen to 50° C. The total distillate collected was 39.5 gms. This mixture had an acidity of 4.48 mgms. KOH/gm. The mixture was then treated with 16 gms. sodium carbonate, 5 gms. sodium chloride in 160 gms. deionized water containing 10 gms. Hydrogen peroxide and then heated to 80°-85° C. and held at 80°-85° C. for 30 minutes. The mixture was allowed to stand without

stirring. The ester component was collected and washed with 160 gms. deionized water containing 5 gms. sodium chloride at 80°–85° C. and allowed to stand and separate. The ester collected weighed 870 gms. This was then vacuum stripped to remove the residual moisture and filtered using filter-aids (such as MAGNESOL from Reagent Chemical & Research, Inc. and HYFLOSUPERCELL CELATOM FW-60 from Eagle-Picher Industries). The dry yield was 850 gms. of a clear liquid.

EXAMPLE 3

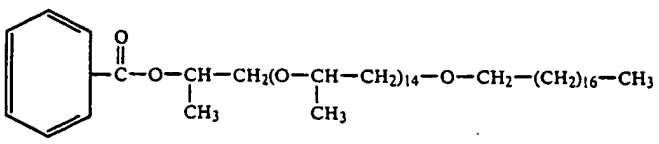
Preparation of Stearoxy-PPG-15 -Benzoate

A mixture of 261 gms. (0.3 moles) of ARLAMOL E from I.C.I. Co. (Propoxylated Stearyl Alcohol, i.e. PPG-15-Stearyl Ether), 42 gms. (0.3 moles) of benzoic acid and 450 mgms. of stannous oxalate was stirred at 27° C. under nitrogen. The mixture was heated to 176° C. over one hour. The mixture was further heated to 230° C. over the next hour at which time distillate started coming off. Further heating was continued and the temperature raised to 250° C. over 30 minutes and held at 250° C. for one hour. The mixture was then heated to 265° C. and held at 265° C. for the next 40–45 minutes and allowed to cool. The reaction mass was then air-cooled to 165° C. Further cooling to 35° C. under nitrogen was accomplished by applying a cooling-water jacket. A clear light yellowish liquid was obtained. The yield for the reaction was 275 gms. Acidity was nearly zero and hydroxyl number was 22.26.

(a) 50 gms. of this ester was treated with 15 gms. deionized water and 0.5 gms. sodium carbonate at 50° C. The mixture was separated and the water layer drained off. The remaining composition was washed with 20 gms. deionized water at 60° C. The ester was then separated and collected and then vacuum stripped at 110° C.–130° C. to remove the residual moisture. The mixture was then cooled to 30° C. and showed slight haze. The liquid was heated with filteraids and filtered at 40° C., using Whatman Filter Paper #42. A crystal clear liquid of benzoate ester emollient was obtained. This clear liquid stayed a clear liquid at 7° C. when refrigerated and did not show any sedimentation or haze.

(b) 170 gms. of this ester was treated with 51 gms. deionized water containing 1.7 gms. sodium carbonate at 50° C. separated and further heated with fresh 68 gms. water at 60° C. The composition was then mixed and allowed to stand for separation. This separated ester was then vacuum stripped at 110°–130° C. and 10–15 mmHg, vacuum cooled to 25°–28° C. and filtered using 0.80 gms. of MAGNESOL and 1–60 gms. HYFLOSUPERCELL (from Johns-Manville Co.) as filter-aids. Filtration was done using Whatman Filter Paper #42. Final product was a clear liquid without odor.

The ester made had the following formula:



The following typical physical and chemical properties were observed:

Specific Gravity @ 24° C.:		0.98
Surface Tension @ 25° C.:		35.1 dynes/cm
Spreading Coefficient @ 25° C.:		31.5 dynes/cm
Pour Point:		−12° C.
Odor:		Bland
Toxicity:	Practically non-irritating (eyes), Primary Skin Irritation Score 0.8,	$LD_5 > 5.0$ g/kg
Appearance:		Clear liquid
Viscosity @ 25° C. (Brookfield #1, 50 rpm):		158 cps

EXAMPLE 4

Preparation of Stearoxy-PPG-15-Benzoate

870 gms. of ARLAMOL E (propoxylated stearyl ether i.e. PPG-15 Stearyl Ether) (I.C.I.) and 50 mgms. sodium borohydride was mixed and heated under nitrogen. The mixture was held at 60° C. for 30 minutes. 140 gms. of benzoic acid and 1–5 gms. stannous oxalate was added. The reaction mixture was then further heated to 200° C. over 30 minutes, and further raised to 240° C. over the next 30 minutes. The reaction was held at 240°–245° C. for 30 minutes and then raised to 265° C. and held at 265° C. for one hour. The distillate collected was 14.5 gms. against theoretical estimates of 14.5 gms. The reaction mixture was cooled to 35°–40° C. under nitrogen. The ester had the acidity of 5–84 mgms. KOH/gms. The reaction product was treated with 360 gms. deionized water containing 16 gms. sodium carbonate, 5 gms. sodium chloride at 80°–85° C. The ester was allowed to stand overnight. The top layer containing the benzoate ester was collected. It weighed 1037 gms. It was vacuum stripped at 115°–120° C. and 10–15 mm Hg vacuum. The liquid benzoate of this reaction weighed 850 gms. which was then treated with 2.25 gms. MAGNESOL and 4.25 gms. CELATOM FW-60 (Diatomaceous earth) at 50° C. and filtered at 50° C. The net yield of the liquid benzoate ester product was 835 gms.

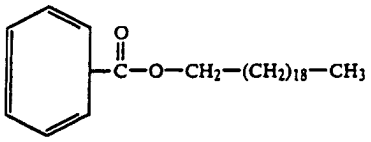
EXAMPLE 5

Preparation of Arachidyl-Benzoate

A mixture of 104 gms. (0.348 moles) of arachidyl alcohol, 46 gms. (0.362 moles) of benzoic acid and 225 mgms. stannous oxalate was heated under nitrogen to 230° C. The reaction was held at 230° C. for two hours under nitrogen. The acidity was 10 mgms. KOH/gms. The mixture was then cooled to 100° C. During the reaction distillate was collected. The ester formed was solid at room temperature and showed solidication at 80° C. The ester was given a treatment at 85° C. with 50 gms. deionized water containing 2 gms. sodium carbonate, 2 gms. sodium chloride and 1 gm. hydrogen peroxide. The mixture was allowed to stand and separate. The top layer was washed with 50 gms. deionized water at 80°–85° C., separated and cooled. The top layer solidified and bottom layer was completely drained off. The

ester was then vacuum stripped at 100°–105° C. The ester so formed was a white solid benzoate.

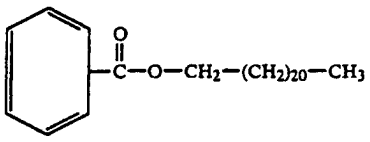
The ester had the following formula:



EXAMPLE 6

Preparation of Behenyl Benzoate

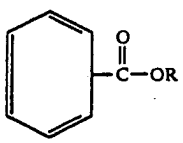
A mixture of 106.5 gms. (0.326 moles) of behenyl alcohol, 43.5 gms. (0.343 moles) of benzoic acid and 225 mgms. stannous oxalate was heated to 230° C. under nitrogen. The reaction was held at 230° C. for two hours, and the distillate collected. It was then cooled to 100° C. The acidity was 10.0 mg KOH/gm. The ester was then given a treatment for 30 minutes at 85° C. with 50 gms. deionized water, 2 gms. sodium carbonate, 2 gms. sodium chloride, and 1 gm. hydrogen peroxide. It was then allowed to stand and the lower aqueous layer drained off. The top layer was washed with 50 gms. water at 80°–85° C. and then separated. The solid was then vacuum stripped at 100°–105° C. to remove residual moisture. The final product was a solid benzoate ester having the following formula:



EXAMPLE 7

Preparation of Benzoate ester of a mixed 20+ Carbon Chain Distribution

A mixture of 155.04 gms. of Epal 20+ alcohol (Ethyl Corporation), 44.96 gms. of benzoic acid and 300 mgms. of stannous oxalate was heated to 228° C. under nitrogen. The distillate was collected during the reaction. The reaction mixture was cooled to 100° C. The acidity was 12 mgms. KOH/gm. 176 gms. of this mixed alcohol benzoate was treated with 65 gms. deionized water containing 2 gms. sodium carbonate, and 1 gm. hydrogen peroxide at 85° C. This mixture was very fluid and the bottom aqueous wash liquid was drained off. The top layer of the subject benzoate ester was further washed with 65 gms. deionized water at 75° C. The composition was allowed to stand and the ester layer removed. The net yield of this mixed alcohol benzoate ester was 120 gms. and the final product was a soft smooth paste at room temperature. The composition had the following formula:



wherein R is a mixture of alky substituents from C_{20} to C_{28}.

EXAMPLE 8

Preparation of Cetoxy-PPG-10-Benzoate

214 gms. Procetyl-10 (Cetoxyl-PPG-10 from Croda, Inc.) and 15 mgms. sodium borohydride were mixed and heated under nitrogen. 36 gms. of benzoic acid and 375 mgms. stannous oxalate were added. Reaction mixture was then heated to 250° C. over ½ hour and held @ 250° C. for the next 1 hour. Additional one hour of reaction time was @ 250° C. Reaction was then cooled to 50° C. under nitrogen. 235 gms. of this crude ester was obtained. This crude ester was treated at 80°–85° C. for ½ hour with 25 gms. water, 2 gms. sodium chloride, 5 gms. sodium carbonate and 5 gms. hydrogen peroxide. Allowed to stand for separation. The ester was separated and given a further wash with 50 gms. water and 1 gm. sodium chloride @ 65°–75° C. Allowed to separate and the ester layer was collected. The ester layer was further washed with 50 gms. water. Allowed to separate and the top hydrous ester layer was collected. The hydrous ester layer was vacuum stripped at 110°–120° C. @ 8–10 mm Hg. vacuum. The liquid benzoate ester of this reaction was then heated @ 35° C. with 0.5% Magnesol and 0.25% Celatom FW-60. The net yield of this benzoate ester was 180 gms.

EXAMPLE 9

Preparation of Butoxy-PPG-15-Benzoate

220 gms. Ucon LB-285 (PPG-15-Butyl ether from Union Carbide) and 15 mgms. sodium borohydride were mixed and heated under nitrogen. 30 gms. benzoic acid and 375 mgms. stannous oxalate were added. Reaction mixture was then heated to 250° C. and held @ 250° C. for 1½ hours. The reaction mixture was cooled to 50° C. and to this was added 1 gm. hydrogen peroxide and then heated to 80°–85° C. for ½ hour. 234 gms. of the crude ester was further treated with 20 gms. water, 2 gms. sodium carbonate and 1 gm. sodium chloride @ 80° C. Allowed to separate @ 80° C. The ester thus separated was then treated with 25 gms. water, and 1 gm. sodium chloride. The top layer was collected and further treated with 25 gm. water and 1 gm. sodium chloride. Allowed to stand and then separated the ester layer which was nearly water-white liquid yet hazy due to some moisture held by the compound. Product of the reaction was vacuum dried @ 10–15 mm. Hg. and 110°–120° C. over 45 minutes and then treated with 0.5% Magnesol and 0.25% Celatom FW-60 and subsequently filtered. The product collected was a clear water-white liquid and weighed 170 gms.

EXAMPLE 10

Foam Tests

Model shampoo formulations comprised of benzoate ester, surfactant, an alkanolamide and water, at concentrations indicated, were investigated for foam properties and characteristics utilizing the technique known as 'Ross-Miles' foaming test. This test procedure, performed at 40±2° C., under the indicated conditions, is a relatively standard foam test in and is readily accepted by the cosmetics and toiletries industries.

Table I shows that the benzoic acid esters of this invention will increase the foam volumes of synthetic detergents (A-E), soaps (F-I) and soap syndets (J-L)

whereas the corresponding alcohol reactant decreases foam volumes.

TABLE I

ROSS-MILES FOAM TEST

Test Conditions: Temperature 40 ± 2° C.; Water Harness 0°H; Test Concentration 0.12% wt/wt.

COMPONENT	(%) A**	B	C	D	E	(%) F**	G	H	I	(%) J**	K	L
Sodium Laureth (3) Sulfate	12.0	12.0	12.0	12.0	12.0	—	—	—	—	—	—	—
Sodium (Tallow) Soap	—	—	—	—	—	12.0	12.0	12.0	12.0	—	—	—
Sodium Cocoyl Isethionate/ Sodium (Tallow) Soap, 1:5	—	—	—	—	—	—	—	—	—	12.0	12.0	12.0
Lauramide DEA	3.0	3.0	3.0	3.0	3.0	—	—	—	—	—	—	—
Octyldodecyl Benzoate (Invention)	—	—	5.0	—	—	—	2.5	—	5.0	—	5.0	2.5
Stearoxy PPG-15 Benzoate (Invention)	—	—	—	—	2.5	—	—	5.0	—	—	—	—
Octyldodecanol	—	5.0	—	—	—	—	—	—	—	—	—	—
PPG-15 Stearyl Ether	—	—	—	5.0	—	—	—	—	—	—	—	—
Water	85.0	80.0	80.0	80.0	82.5	88.0	85.5	83.0	83.0	88.0	83.0	85.5
pH	6.5	6.4	6.4	6.2	6.6	9.8	10.0	9.8	9.7	9.7	9.4	9.7
Results*	155/ 150	145/ 140	165/ 155	125/ 110	160/ 150	150/ 150	170/ 170	160/ 158	175/ 175	155/ 155	165/ 165	170/ 167

*represented as mm foam @ t = 0/mm foam @ t = 5 min
**Controls
% by weight

EXAMPLE 11

Use of compounds in cosmetic and toiletry compositions, particularly aqueous surfactant compositions

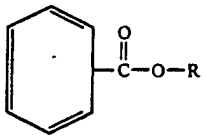
Soap Based Shampoo	% wt/wt	Synthetic Detergent Based Shampoo	% wt/wt
"Neat Soap"*	20.0	Sodium Laureth Sulfate	12.0
Sodium Cocoyl Isethionate	2.0	Lauramide DEA	3.0
Octyldodecyl Benzoate	2.5	Stearoxy-PPG-15 Benzoate	2.5
Water	75.5	Water	82.5
Color	q.s.	Color	q.s.
Fragrance	q.s.	Fragrance	q.s.

*approximately 30% water.

Each shampoo produces greater foam volume than similar shampoos not having the benzoic acid esters.

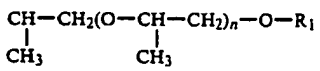
What is claimed is:

1. A method of modifying while not suppressing foam in an aqueous surfactant composition comprising admixing with the aqueous composition a foam modifying amount of a substantially pure benzoate ester composition of the formula:



wherein

R is



wherein n is 9–16 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms.

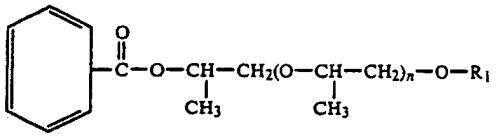
whereby the foam is modified but not suppressed.

2. The method of claim 1, wherein n is 14.

3. The method of claim 2, wherein R_1 is $C_{18}H_{37}$.

4. The method of claim 2, wherein R_1 is C_4H_9.

5. A benzoate ester of the formula:



wherein n is 9 to 16 and R_1 is a branched or linear alkyl of 3 to 22 carbon atoms.

6. The ester of claim 5, wherein n is 14.

7. The ester of claim 6, wherein R_1 is $C_{18}H_{37}$.

8. The ester of claim 6, wherein R_1 is C_4H_9.

9. The ester of claim 5, wherein R_1 is $C_{16}H_{33}$.

10. The ester of claim 9, wherein n is 9.

* * * * *

EXHIBIT - 2

US006635775B1 EV 447666251

(12) **United States Patent**
Walele et al.

(10) **Patent No.: US 6,635,775 B1**
(45) **Date of Patent: Oct. 21, 2003**

(54) **REDUCED ODOR ESTERS AND PROCESS FOR PRODUCING SAME**

(75) Inventors: **Ismail Walele**, Saddle Brook, NJ (US); **Samad A. Syed**, Paramus, NJ (US)

(73) Assignee: **Finetex, Inc.**, Elmwood Park, NJ (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/498,565**

(22) Filed: **Feb. 4, 2000**

Related U.S. Application Data

(60) Provisional application No. 60/118,977, filed on Feb. 8, 1999.

(51) **Int. Cl.**[7] **C07C 51/42**; C07C 53/00; C07C 69/76; C07C 67/48

(52) **U.S. Cl.** **554/175**; 554/176; 554/182; 554/227; 560/103; 560/112; 560/248

(58) **Field of Search** 560/103, 112, 560/248; 554/175, 176, 182, 227

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Yoshino et al, Synthetic studies with carbonates. Part 6. Syntheses of 2–Hydroxyethyl Derivatives by Reactions of Ethylene Carbonate with Carboxylic Acids of Heterocycles, 1977, Journal of the Chemical Society, Perkin I, (11), pp. 1266–1272.*

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(57) **ABSTRACT**

An improved process for preparing reduced-odor or odorless esters, preferably benzoate esters, octanoate esters, aliphatic emollient esters and glycol dibenzoate esters. The improved process comprises, in part, removing the esterification catalyst from the crude ester after the esterification reaction is substantially complete, before neutralization of acidity. The resultant ester compositions are odorless or have substantially reduced odor as compared to commercially available esters.

43 Claims, No Drawings

REDUCED ODOR ESTERS AND PROCESS FOR PRODUCING SAME

This application claims benefit of U.S. Ser. No. 60/118,977 filed Feb. 8, 1999.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to reduced odor or odor-free esters, and more particularly to odor-free C12–C15 alkyl benzoate esters, octanoate esters, glycol dibenzoate esters, and other emollient esters, their process of manufacture and their use in cosmetics and personal care products as carriers or vehicles, or a diluents, solvents, plasticizers, emollients and solubilizers.

2. Description of the Related Art

Esters are known for a variety of different applications for cosmetic, pharmaceutical and medicinal purposes.

Numerous references describe the production and use of benzoic acid esters. None of these references teach or suggest the specific novel reduced odor or odorless benozate esters of this invention or the use of these and other reduced odor benzoate esters in cosmetics and personal care products.

For example, benzoate esters of certain alcohols and alcohol mixtures and their uses are disclosed in assignee's U.S. Pat. Nos. 4,323,694; 4,322,545; and 4,275,222, all to Scala; and U.S. Pat. Nos. 4,791,097; 5,270,461; and 5,271,930, all to Walele et al. The disclosures of these patents are incorporated herein by reference.

U.S. Pat. Nos. 4,323,694; 4,322,545; and 4,275,222 to Scala disclose benzoic acid esters and processes for making same, using methane sulfonic acid as a catalyst at temperatures of about 160° C. to 175° C. The catalyst containing crude ester is washed and dried. Although there is no specific teaching of such washings in Scala, the industry practice is to neutralize any residual acidity with an alkali water wash. The ester is then further washed, as necessary, and dried. The Scala patents do not disclose using stannous oxalate as a catalyst, running the reaction at very high temperatures (220° C. or more), or removal of the catalyst as a process improvement to improve the odor of the resultant esters.

U.S. Pat. Nos. 4,791,097; 5,270,461; and 5,271,930 to Walele et al. disclose benzoic acid esters and processes for making same. The processes disclose reacting benzoic acid with an alcohol, using a catalyst, heating and then cooling, and collecting distillate. The mixture was subsequently treated with, among other things, hydrogen peroxide, and heated at 80° C.–100° C. The ester component was collected, washed with neutralization, and then refined by washing and drying.

U.S. Pat. No. 2,997,494 to Brown discloses a method of preparing vinyl esters of carboxylic acids.

U.S. Pat. No. 3,843,719 to Brady discloses a process for preparing esters of carboxylic acids.

U.S. Pat. No. 4,304,925 to Watanabe et al. discloses a process for obtaining esters by reacting an organic carboxylic acid or its anhydride with an alcohol in the presence of an organometallic compound as a catalyst. There is no recognition of steps taken specifically to improve the odor of the esters.

U.S. Pat. No. 4,506,091 to Deardorff discloses a method for refining esters without the necessity of washing procedures. Improvement of the odor of the ester is not contemplated or recognized.

U.S. Pat. No. 5,302,746 to Koono et al. discloses a process for producing a carboxylic acid ester, using a countercurrently contacting column for neutralization.

U.S. Pat. No. 5,693,316 to Pereira et al. discloses fatty alkoxylate esters of aliphatic and aromatic dicarboxylic acids.

U.S. Pat. No. 5,783,173 to Bonda et al. discloses a sun-screen composition containing a UV-B dibenzoylmethane derivative such as PARSOL 1789, and a stabilizer/solubilizer for the dibenzoylmethane derivative, and mixtures thereof.

However, among the foregoing patents, none have the unique properties of the ester compositions described and claimed herein. None disclose or suggest a process for the production of esters and emollient esters which are odorless or which have extremely low odor due to the absence of odor-causing species such as aldehydes, carbonyl compounds, and the like. This is a vital property in numerous applications, as the esters may be incorporated into personal care products, where absence of odor is critical to consumer acceptance.

This is due in part to the failure of prior processes to recognize that removal of the catalyst improves the odor, and to the use of certain unsuitable catalysts. For instance, the Scala patents referred to above use Methane Sulfonic Acid (MSA) as a catalyst. The problem with using MSA as a catalyst is that it is soluble in the organic reactants. MSA dissolves in the organic matter during reaction and cannot be physically removed by filtration from the reaction mix. It is not heterogeneous as is the case with stannous oxalate and metal oxides. However, it is neutralized in the neutralization/washings which follow subsequent to the esterification reaction. So even after neutralization and washing, odorous esters are formed because the intrinsic odor from the raw materials remains. Another problem with MSA is that the reaction cannot be run at high temperatures; exceeding temperatures of about 170° C. to 175° C. results in formation of chocolate-colored organic matter. It has been found by applicants that the darker the ester product, generally the worse the odor. Esters made using MSA as a catalyst have been found by applicants to be odorous.

In developing formulations for personal care products, it is critical to utilize a product that lacks odor. Many emollients have a characteristic obnoxious odor that is difficult to mask. Masking odors is an inordinately difficult and expensive task. Known methods of producing esters and ester-emollients result in esters which are odorous, i.e., they have an MFL, a minimum fragrance level. This is a disadvantage because perfumes must then be added to mask or overcome the MFL. Additionally and/or alternatively, the esters are deodorized by various methods including filtering, bleaching clays, or steam distilling the esters. Masking the obnoxious odors of many emollients is both difficult and expensive.

The disadvantages of the known methods of producing esters and emollient esters are overcome by the process of the present invention. Unexpectedly, the esters of the invention are odorless or have a very small MFL, avoiding the need for perfumes and deodorization.

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process or producing esters and emollient esters which have a low odor, or MFL, or which are odorless, due to the absence of odor causing species such as aldehydes, carbonyl compounds, and the like.

It is another object of the invention to provide a process for making reduced odor or odorless esters and emollient esters for use in cosmetics and personal care products.

It is yet another object of the invention to provide a process for making reduced odor or odorless esters and emollient esters for use in products where the addition of perfumes is objectionable.

It is a further object of the invention to provide a process for making esters and emollient-esters for use in cosmetics and personal care products which reduces the need for perfumes in cosmetics and personal care products.

Yet another object of the invention is to provide a method for producing esters and emollient esters which obviate the need for extraneous filtration or deodorizing techniques to remove odor.

Another object of the invention is to provide a method of producing reduced odor or odorless cosmetics or personal care products using certain specific benzoic acid esters.

It is another object of the invention to provide low-odor or non-odorous esters and emollient esters by reducing or substantially eliminating odor causing species.

Yet another object of the invention is to provide novel esters which may serve as emollient's and which may also modify the odor characteristics of the products in which they are used.

It is another object of the invention to provide reduced odor or non-odorous esters and ester emollients for use in products where the use of perfumes is objectionable.

It is another object of the invention to provide reduced odor or non-odorous esters and ester emollients for use in cosmetics and personal care products to reduce the use of perfumes in these products.

Yet another object of the invention is to provide esters and ester emollients for use in products where the odor of the ester may interfere with that of other ingredients.

These and other objects are accomplished by providing an improved process for preparing reduced-odor or odorless esters, preferably benzoate esters, octanoate esters, aliphatic emollient esters and glycol dibenzoate esters. The improved process comprises, in part, removing the esterification catalyst from the crude ester after the esterification reaction is substantially complete, before neutralization of acidity. The resultant ester compositions are odorless or have substantially reduced odor as compared to commercially available esters.

DESCRIPTION OF THE INVENTION

The novel esters of this invention have unique properties in that they have reduced odor or are substantially odor-free. This property makes the compositions useful as a vehicle or carrier, emollient or solubilizer for toiletry and cosmetic formulations and personal care products, such as hair creams, hand cleaners, bath oils, suntan oils, antiperspirants, perfumes, colognes, cold creams, electric preshaves, eye and throat oils, finger nail polish, topical pharmaceutical ointments, lipsticks, stick rouge, skin lotions and creams, skin moisturizers, cleansing creams, and after-bath splash and lotions, as well as other formulations. The foregoing list is only exemplary of the type of compositions in which the esters of this invention may be used, and, as such, is not to be considered limiting.

DETAILED DESCRIPTION OF THE INVENTION

The odor-free emollient esters produced by the process of the invention include:

a. Benzoate Esters in general, and C12–15 Alkyl Benzoate Esters in particular, as set forth in Example Nos. 1 through 11 below;

b. Octanoate Esters, and in particular, aliphatic cetearyl octanoate esters, as set forth in Example Nos. 12, 13, and 27 below.

c. Aliphatic.emollient esters, specifically, C12–15 Alkyl Octanoate Esters, as set forth in Example Nos. 14, 15, 25 and 26, below;

d. Glycol Dibenzoate esters, specifically Dipropylene Glycol Dibenzoate, as set forth in Example Nos. 16 and 17, below.

The preferred alcohol precursors used in preparing the odor-free benzoic acid esters of the invention are selected from the group consisting of alcohols containing from 3 to 22 carbon atoms, and preferably C12–C15 alcohols. Typical examples include octyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, behenyl alcohol, oleyl alcohol, isostearyl alcohol, arachidyl alcohol, etc. The preferred alcohol is Neodol 25 (Shell Chemical Company).

The odor-free octanoate esters of the invention are obtained by reacting ethylhexanoic acid with an alcohol in accordance with the process of the invention. The alcohol is selected from the group consisting of alcohols containing from 3 to 22 carbon atoms, and preferably C12–C15 alcohols. Typical examples include octyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, behenyl alcohol, oleyl alcohol, isostearyl alcohol, arachidyl alcohol, etc. The preferred alcohol is Neodol 25 from Shell Chemical Company.

The odorless aliphatic emollient esters of the invention are made by reaction of alcohols and carboxylic acids in accordance with the process of the invention. The alcohols may be alcohols such as those comprising 3 to 22 carbon atoms, e.g., octyl alcohol, decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, arachidyl alcohol, behenyl alcohol, isostearyl alcohol, etc. Preferably, the alcohol is a C12–C15 alcohol. Most preferably, the alcohol is Neodol 25 from Shell Chemical Co. The carboxylic acids may be selected from the group of carboxylic acids consisting of linear or branched, with 4 to 22 carbon atoms, such as octanoic acid, decanoic acid, ethylhexanoic acid, lauric acid, myristicacid, palmitic acid, stearic acid, oleic acid, behenic acid, isostearic acid and arachidic acid.

The odor-free glycol dibenzoate esters of the invention are prepared by reacting a glycol with benzoic acid in accordance with the process of the invention. The glycol comprises from 3 to 12 carbon atoms, preferably 6 to 12 carbon atoms. Most preferably, the glycol is dipropylene glycol.

The foregoing list is only exemplary of the type of precursors on which the emollient esters may be based, and, as such, is not to be considered limiting.

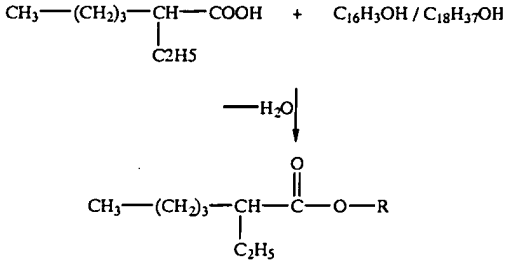
In a specific embodiment, and by way of illustration, this invention contemplates the production of low odor or odorless emollient-esters in accordance with the following equation:

A. Octanoate Ester Chemistry

FINESTER CST-8, also known as cetearyl octanoate, is a branched chain emollient ester; FINESTER EH-25 is an octanoate ester of C12–15 alcohol.

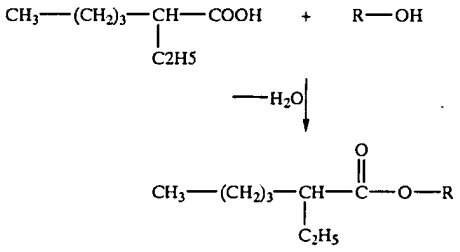
In the following discussion, FINESTER CST-8, FINESTER EH-35, FINSOLV PG-22, and FINSOLV TN are registered trademarks of Finetex, Inc., Elmwood Park, N.J., 07407.

Reacting 2-Ethyl Hexanoic Acid+C16–18 Alcohol (may be Cetyl or Stearyl Alcohol) in the presence of a catalyst produces Cetyl/Stearyl/Ethyl Hexanoate (also known as Cetyl/Stearyl Octanoate).



Where R=C_{16}–C_{18} Alkyl (sold as FINESTER CST-8)

Reacting 2-Ethyl Hexanoic Acid+C12–15 Alkyl Alcohol in the presence of a catalyst produces C12–15 Alkyl Ethyl Hexanoate (also known as C12–15 Alkyl Octanoate), as follows:



Where R=C12–15 Alkyl (Sold as FINESTER EH-25)

The odor-free, emollient benzoate esters of this invention are produced by reacting benzoic acid with an alcohol, as is known in the art, and as taught in the Scala and Walele et al. patents, supra. A catalyst is present during the reaction. The process for preparing the esters is preferably a batch process, but may also be a continuous process, for instance, conducted in a continuous extractor.

Superior, reduced odor or odorless esters are produced in part by removing the catalyst from the mass after the reaction is complete and before neutralization. The catalyst is preferably removed by filtration so that the crude ester mass is free of the catalyst particulate matter. Thereafter, the crude ester is worked up by neutralizing, washing and drying. The resultant processed refined ester is odorless or practically odorless as compared to prior art esters.

Applicants have discovered that removal of the catalyst from the mass after the reaction is complete and before neutralization has multiple benefits. These include reducing the use of alkalis for neutralization of organic acidity, thus reducing the formation of oxalic acid neutral species. Another benefit is reducing loss during the washing procedure by way of reducing the amount of inseparable emulsion phase (interphase) which causes loss of product, thus improving the yield. Removing the catalyst before neutralizing and washing the crude ester improves the yield and odor of the resultant ester and results in a sharp separation during the washing.

Thus, applicants have found that removal of the catalyst advantageously prevents the occurrence of undesirable side reactions which may interfere with formation of the desired esters. In the case of stannous oxalate as the catalyst, these undesirable side reactions include effects of alkalis on alcohol or ester, in the presence of stannous oxalate; the reaction of stannous oxalate with hydrogen peroxide to form oxalic acid; and oxidation of unreacted alcohol to aldehyde and ketone in the presence of hydrogen peroxide and stannous oxalate.

Another factor in reducing odor is the use of sodium borohydride for the treatment of the alcohol., i.e., C12–15 alcohol, before reacting with Benzoic Acid and before contacting the mixture of reactants and catalyst, to convert aldehyde and other species in the reaction to alcohol. Use levels of sodium borohydride can be from 10 ppm to 500 ppm.

Other starting alcohols or glycols (besides C12–15 alcohols), such as dipropylene glycol or C16–C18 alcohol, may be pretreated with sodium borohydride, but it is not a requirement of the process of the invention to do so. As shown in Example No. 1 below, Neodol 25 (Shell Chemical Company) is not pretreated with Sodium Borohydride, yet good odor results were obtained even without pretreatment. This is thought to be due to the fact that in this Example where the catalyst was removed, and hydrogen peroxide was not used in any step during the reaction and washing, there is such a minute amount of impurities in the form of aldehydes and ketones that, even without using sodium borohydride, the odor is very good. While the color of the ester is slightly higher, it is still good (less than 20 APHA).

In contrast, as can be seen from Example #2 below, when the starting alcohol was not pretreated with sodium borohydride, and the catalyst was not removed, and hydrogen peroxide was added to the crude ester before the washing step, the resulting ester had a mild to strong odor, there was a loss of yield in the form of increased interphase, but the resulting ester had very good color.

As demonstrated in Example #4 below, where the alcohol is pretreated with sodium borohydride, the catalyst is removed from the reaction mass, and hydrogen peroxide is added before neutralization of acidity, the resulting ester has a mild odor, there is loss of some yield, and the ester has a good color.

In summary, esters with the best odor and yield are obtained is where there is no pre-treatment with sodium borohydride, the catalyst is removed, and hydrogen peroxide is not added, as demonstrated in Example #1. Esters having adequate, but not as good, odor and yield, are obtained where there is no pre-treatment with sodium borohydride, the catalyst is removed, and hydrogen peroxide is added before neutralization in aqueous form, as demonstrated in Example #4. Esters having the worst odor and yield were obtained when there was no pretreatment with sodium borohydride, the catalyst was not filtered, and hydrogen peroxide was added to the anhydrous crude ester, as demonstrated in Examples #29 and #30 below. See Table III for comparative results.

The catalyst may be selected from the group consisting of stannous oxalate and metal oxides, such as zinc oxide. Stannous Oxalate is a catalyst in the category or group of Organometallics. It is also referred to as an organotin catalyst. Stannous Oxalate may be used in the range of 0.05% to 1.5% on the weight of the alcohols. Metal oxides in general, and zinc oxide in particular, may be used as catalysts in the range of 0.1% to 1.0% on the weight of the alcohols.

The preferred catalyst is Stannous Oxalate, which is insoluble in the reaction mixture, in the alcohol alone, or in the carboxylic acid alone. The advantage of using this catalyst is that it can be filtered or removed by other means from the crude ester. Methane sulfonic acid is not used as a catalyst because it cannot be physically removed by filtration or otherwise easily removed from the crude ester, unless it is washed.

The catalyst is removed from the crude ester after the reaction is complete and before neutralization. The reaction is deemed complete when the acid value is less than 10 mg KOH/g.

The reaction mixture may optionally be cooled to room temperature before removing the catalyst, preferably by filtration. Filtration may be accomplished by any conventional means, including using cartridges, filter strainers, filter press, or centrifuge. Thus, the products containing stannous oxalate and zinc oxide as catalysts are filtered to remove the heterogenous catalyst.

The next step is neutralization/washing of the optionally cooled crude ester which has been filtered. The crude ester with its acidity of no more than 10 mg KOH/g is neutral washed with stoichiometric, or slightly greater than stoichiometric, amounts of alkalis. This guarantees that acidity of the crude ester is overcome. This can optionally be verified by testing for acid value in the top layer of the mix. An acid value of 0 indicates that acidity has been completely neutralized. The alkalis can be sodium or potassium salts such as carbonates or hydroxides. The quantity of wash water can be from 1% to 25% on the weight of crude filtered ester. Sulfate salts or chloride salts of sodium or potassium are used at levels of 1% to 25% on the weight of total waters used for neutralization and/or washing. Thus, the optionally cooled but filtered crude ester is washed with neutralizing solutions containing an alkali metal carbonate to neutralize acidity of the catalyst and reactants, and sodium chloride or sodium sulfate. The sodium chloride or sodium sulfate salts are added for the purpose of phase separation of the two-phase systems of neutralizing/washing mixtures, i.e., the aqueous and organic phases. Phase separation is done at a temperature of 20° C. to 100° C., preferably between 40° C.–100° C., and more preferably between 60° C.–100° C.

After neutralization is complete, as evidenced by zero acidity and minor alkalinity, which assures acidity has been neutralized, then a certain quantity of hydrogen peroxide is added to the same first wash containing crude ester, water, sodium carbonate, and sodium sulfate, for the purpose of treating the ester, and especially for the purpose of bleaching the ester. If hydrogen peroxide is added before neutralization is complete, an odorous ester will result. The degree of odor depends on the stage of completion of neutralization. The more complete the neutralization of acidity, the better the odor of the resultant ester.

The concentration of hydrogen peroxide in its 30%–35% commercially available strength is in the range of 0.02% to 2.0% on the weight of the crude ester. This translates to a range of 6 ppm to 7000 ppm levels of hydrogen peroxide. Hydrogen peroxide is added to bleach the slight darkening in the reaction mixture.

The crude ester is in contact with hydrogen peroxide only in its abundantly wet form, i.e., only in the presence of large quantities of wash water or neutralization wash waters. Thus, if it is desired to bleach the reaction mixture with hydrogen peroxide, the treatment with hydrogen peroxide is done during the alkaline wash, but after the alkalines are entered and have neutralized the acidity, rather than in the anhydrous form of the crude ester. The use of hydrogen peroxide on the anhydrous crude ester at elevated temperature is believed to give or impart an odor to the composition which does not diminish subsequently, during the washing processes, as demonstrated by Ex. #29 below.

If the hydrogen peroxide is added simultaneously, i.e., in one step, with the neutralization or wash waters, as taught in the '097 and '461 Patents to Walele et al., supra, there is no improvement in the odor or color of the resultant ester. However, applicants have discovered that if the catalyst is removed, and hydrogen peroxide is added sequentially to the neutralization or wash waters, after neutralization is complete, esters having improved odor, color and yield are obtained.

In other words, it is not required in the invention process to add hydrogen peroxide. However, it is sometimes desirable to add hydrogen peroxide to improve (whiten) the color of the resulting ester. If it is desired to add hydrogen peroxide, it must be added after neutralization is complete, during the washing step, or after the washing step, while the ester is still wet, to eliminate or significantly reduce the odor of the resulting ester.

The process of the invention uses hydrogen peroxide in the aqueous washings (after neutralization is completed) to avoid contacting the anhydrous crude ester with hydrogen peroxide. Preventing hydrogen peroxide from contacting the anhydrous crude ester avoids the oxidation, if any, of the organic unreacted matter of the reaction mass. This prevents imparting an odor to the ester which cannot be washed out later.

Applicants have found that when hydrogen peroxide is added after neutralization of the acidity, the odor of the resulting ester is much improved, especially when the catalyst is removed. Applicants theorize this is because the chances of other side reactions occurring are negligible. For instance, the oxidation of alcohol to aldehydes, which typically creates odorous compounds, does not occur. This was not the case with prior art processes, such as that taught by U.S. Pat. No. 4,791,097 to Walele et al. In the '097 Patent, water, salt, sodium carbonate and hydrogen peroxide were added together simultaneously, without filtration of the catalyst, before neutralization of the acidity. The resultant ester has a strong odor, dark color, and poor yield, as shown in Example #31, below.

Applicants have found that odorous esters are formed when the anhydrous crude ester comes into contact with hydrogen peroxide at high temperatures of 80° C. to 100° C. in the presence of a catalyst, such as stannous oxalate.

It is preferred to have a second wash to remove alkalinity. The alkalinity is-removed easily by washing with water containing a salt, such as sodium sulfate or sodium chloride. The wet ester so obtained may also be subjected to a third wash of water and salt to insure no alkalinity remains. Then the wash water is removed.

The wet ester is contacted with hydrogen peroxide after neutralization is completed, in the same wash bath with the products of neutralization. Alternatively, hydrogen peroxide may be added separately, in a subsequent wash, after removal of the first wash water, following phase separation, while the ester is still wet and after neutralization is complete.

The next step is drying of the esters. The washed ester is subjected to drying at 100° C.–120° C. under reduced pressure of up to 1–5 mm Hg and until the residual moisture is less than 0.05%.

A final filtration step follows. The dry ester is filtered using diatomaceous earth filter aids.

Thus, applicants have found that removal of the catalyst before neutralization washing of the acidity with alkali, followed by drying of the ester, will result in odorless ester with some color. For exceptional color, hydrogen peroxide may be added to the filtered crude ester after neutralization of acidity and before drying in low pressure. There should not be any free hydrogen peroxide in the system. This will make possible the production of very low odor to odorless esters with good color.

Where the catalyst is not removed and hydrogen peroxide is added, the resultant ester has good color, but is odorous. Simply removing the catalyst and not adding hydrogen peroxide results in esters which are odorless and have some color. Removing the catalyst and adding hydrogen peroxide results in esters which are odorless and have good color, i.e., very low color.

Thus, the advantages provided by this invention are primarily production of an odorless ester, and improvement in the color and yield of the ester.

The benzoate esters of this invention may be used in skin care and personal care compositions. The amount used in skin care compositions is dependent on the type of skin care composition, the type and quantity of other ingredients, such as cosmetic ingredients used, and the amount and type of functional additives that are utilized. Typically, the amount of benzoate ester used ranges from about 0.5% to about 80%, by weight, of the skin care compositions. For example, a facial cream may only have about 0.5%, while a massage oil may have up to about 80% by weight.

Still higher amounts may be used in, for example, bath oils, e.g. 95%.

Further, the benzoate esters of this invention possess other unusual physio-chemical properties, which can make them suitable for use as emollient carriers in cosmetic formulations, and for use as solvents and emollient carriers in general cleaning compositions, such as in hand, face, and body creams and lotions. Thus, the benzoate esters described herein may serve not only as emollients and carriers, but may also exhibit one or more other functions.

The benzoic acid esters and emollient esters of the invention have properties in common with the C12–C15 benzoate and other esters of the prior art, such as the '545 Patent to Scala, in terms of being less greasy, less oily having low cloud point and pour points, low toxicity, ease of emulsification, high spreading coefficient, acid and alkaline stability, the ability to form gels with suspending agents, water solubility/dispersibility, and the ability to act as solvents for many common skin and hair care ingredients. This is because the process of the invention utilizes the same starting or raw materials as the '545 Patent to Scala, but uses a different process to produce the esters. The process of the invention results in the production of esters having improved odor and color, and greater yields, as compared to the esters of the '545 Patent to Scala. The improved yield is a further benefit of the process of the invention; by removing the catalyst there are less impurities to be washed, and no side reactions occurring during washing.

The following are non-limiting examples of processes for preparing the ester compositions of the invention and comparative examples of processes for preparing ester compositions of the prior art (Examples 1 to 31); uses of the compositions in specific cosmetic or personal care product formulations wherein the property of reduced or no fragrance is useful (Examples 32 to 35); and odor panel test results (Examples 36 to 37). In the Examples, as well as throughout this application, the chemical and scientific symbols have their customary meanings and all percents are weight percents unless otherwise specified.

Example Nos. 1 through 31 identify esters produced by the old process, and the new process of the invention. For ease of identification, each ester is identified by both an Example Number and a Reference No., where applicable. This identification system is used in the subsequent Tables III, III-A, III-B, III-C and III-D.

By "other process" in the Examples below, and the corresponding Tables, unless otherwise specified, is meant a process of the prior art as described, using FINESOLV TN® available from Finetex, Inc. as the raw material, wherein the catalyst is not removed during the reaction before neutralization and washing. Unless otherwise specified, it is not intended to refer to the exact process taught in the '545 Scala patent, as Scala teaches use of MSA as a catalyst, and the invention contemplates use of stannous oxalate or zinc oxide as the catalyst. Furthermore, Scala teaches reacting MSA at a lower temperature than the stannous oxalate catalyst is reacted at in the process of the invention. Color in the Examples below is measured using ASTM D-1209 on the APHA scale of the American Public Health Association. APHA scores less than 20 denote good color, with scores of 5 to 10 signifying superior color, i.e., clear color or absence of color. APHA scores over 20 are not good, as a yellow tint is visible, becoming progressively more colored as the APHA scores increase.

BENZOIC ACID ESTER COMPOSITIONS

EXAMPLE #1 (115-178)

Preparation of C_{12-15} Alkyl Benzoate by New Process

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 368.1 grams (1.805 moles) of Neodol 25 (Shell Chemical Company) and 225.54 grams (1.850 moles) of Benzoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C., added 0.84 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over 1 hour. The reaction mixture was then raised to 240° C. in the next 2 hours and held for 1 hour over a vacuum of 28" Hg. The distillate (water of reaction) collected was 32 grams against theoretical estimates of 33.2 grams. The ester had the acidity of 3.4 mg KOH/g. The reaction mixture was cooled to 40° C. under nitrogen and filtered on Buckner Funnel with Whatman Paper #1 to remove any residual Stannous Oxalate. To the 400 grams filtered crude ester, added pre-dissolved 2.0 grams Sodium Chloride and 1.28 grams Sodium Carbonate in 64 grams water. Heated the mixture to 80° C. A sharp separation was observed upon standing for an hour with a small amount of interphase of approximately 3 grams. The wash procedure was repeated two more times with predissolved 1.28 grams Sodium Chloride in 64 grams of water. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual 10 moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. under nitrogen and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	391 grams
% Yield:	97.75
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water %:	0.02
Refractive Index:	1.4850
Color:	<15 APHA
Saponification Value:	182 mg KOH/g
Odor:	Odorless

Example #1 demonstrates production of a superior, odorless ester due merely to the removal of the catalyst, even without pretreatment of the alcohol with sodium

borohydride, and even when no hydrogen peroxide was added. The color of the resultant ester is a slightly darker shade, but still within the very acceptable range for color, i.e., APHA less than 20.

EXAMPLE #2 (112-51)

(Preparation of C_{12-15} Alkyl Benzoate by Other Process)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 368.1 grams (1.805 moles) of Neodol 25 (Shell Chemical Company) and 225.54 grams (1.850 moles) of Benzoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 0.84 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over 1 hour. The reaction mixture was then raised to 240° C. in the next 2 hours and held for 1 hour over a vacuum of 28" Hg. The distillate (water of reaction) collected was 32 grams against theoretical estimates of 33.2 grams. The ester had the acidity of 3.0 mg KOH/g. The reaction mixture was cooled to 100° C. and added 2 grams of 35% Hydrogen Peroxide. The resulting improved color ester was cooled to 40° C. To the 400 grams crude ester added pre-dissolved 2.0 grams Sodium Chloride and 1.28 grams Sodium Carbonate in 64 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with a big amount of Interphase of approximately 18 grams. The wash procedure was repeated two more times with predissolved 1.28 grams Sodium Chloride in 64 grams of water. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	380 grams
% Yield:	95.00
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water %:	0.03
Refractive Index:	1.4847
Color:	<5 APHA
Saponification Value:	181.5 mg KOH/g
Odor:	Mild to strong odor. Not an odorless product

Example #2 is the same as Example #1, with the exception that the catalyst is not removed, and hydrogen peroxide is added to the anhydrous crude ester. The resulting odor has a mild to strong odor due to oxidation of the alcohol to aldehyde in the presence of peroxide and stannous oxalate.

EXAMPLE #3 (121-190)

(Preparation of C12–15 Alkyl Benzoate by Invention Process)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 372.0 grams (1.805 moles) of Neodol 25 (Shell Chemical Company) pretreated with Sodium Borohydride (500 ppm) and 228 grams (1.850 moles) Qf Benzoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 0.84 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over 1 hour. The reaction mixture was then raised to 240° C. in next 2 hours and held for 1 hour over a vacuum of 28" Hg. The distillate (water of reaction) collected was 32 grams against theoretical estimates of 33.2 grams. The ester had the acidity of 3.5 mg KOH/g. The reaction mixture was cooled to 40° C. and filtered on Buckner Funnel with Whatman Paper #42 to remove any residual Stannous Oxalate. To the 400 grams filtered crude ester added pre-dissolved 2.0 grams Sodium Chloride and 1.28 grams Sodium Carbonate in 64 grams water. Heated the mixture to 80° C. A sharp separation was observed upon standing for an hour with a small amount of interphase of approximately 2.5 grams. The wash procedure was repeated two more times with pre-dissolved 1.28 grams Sodium Chloride in 64 grams of water. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	385 grams
% Yield:	96.25
Appearance:	Clear liquid
Acid Value:	0.008 mg KOH/g
Water %:	0.01
Refractive Index:	1.4850
Color:	<20 APHA
Saponification Value:	180.22 mg KOH/g
Odor:	Practically odorless

Example #3 demonstrates production of a practically odorless ester having good color, where the alcohol was pretreated with sodium borohydride, the catalyst was filtered out, and no hydrogen peroxide was added.

EXAMPLE #4 (112-141)

(Preparation of C_{12-15} Alkyl Benzoate by Other Process)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 368.1 grams (1.805 moles) of Neodol 25 (Shell Chemical Company) pretreated with Sodium Borohydride and 225.54 grams (1.850 moles) of Benzoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 0.84 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over 1 hour. The reaction mixture was then raised to 240° C. in next 2 hours and held for 1 hour over a vacuum of 28" Hg. The distillate (water of reaction) collected was 31.2 grams against theoretical estimates of 33.2 grams. The ester had the acidity of 3.3 mg KOH/g. The reaction mixture was cooled to 100° C. and added 2 grams of 35% Hydrogen Peroxide. The resulting improved color ester was cooled to 40° C. To the 400 grams crude ester added pre-dissolved 2.0 grams Sodium Chloride and 1.30 grams Sodium Carbonate in 64 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with a reasonable amount of interphase of approximately 14 grams. The wash procedure repeated two more times with pre-dissolved 1.28 grams. Sodium Chloride in 64 grams of water. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	384 grams
% Yield:	96.0
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water %:	0.025
Refractive Index:	1.48450
Color:	<5 APHA
Saponification Value:	180.6 mg KOH/g
Odor:	Mild odor but not an odorless product

EXAMPLE #5 CR

(Preparation of C_{12-15} Alkyl Benzoate by Invention Process)

A 10,000-lb. batch of FINSOLV TN was made in the plant on commercial scale by following the procedure of Example #3, including pretreatment with sodium borohydride. One gallon of sample was withdrawn from the reactor after the reaction showed acidity <3.0 mg KOH/g. This anhydrous crude ester before Hydrogen Peroxide treatment and washing has haze in it, with light yellow color. Upon standing, the Stannous Oxalate settled in the bottom of the jar, but still the product was not crystal clear. Upon mixing and filtering through Buckner Funnel on Whatman Paper #4 the product became clear liquid. This crude ester was used in the following examples. Note that the liquid of;Ex. #5 CR is unfiltered. In some of the following examples, the liquid of Ex. 5 CR is subsequently filtered.

EXAMPLE #5 (115-172)

(Preparation of C12–15 Alkyl Benzoate by Invention Process)

To 600 grams unfiltered crude ester of Example #5 CR added pre-dissolved 3.0 grams Sodium Chloride and 1.2 grams Sodium Carbonate in 96 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with interphase of approximately 53 grams. The wash procedure was repeated two more times with pre-dissolved 3.0 grams Sodium Chloride in 96 grams of water and in both cases separation was sharp, with approximately 2 to 3 grams of interphase found. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	560 grams
% Yield	93.33
Loss During Washing % :	6.67
Appearance:	Clear liquid
Acid Value:	0.02 mg KOH/g
Water %:	0.02
Refractive Index:	1.4850
Color:	<20 APHA
Saponification Value:	181.66 mg KOH/g
Odor:	Odorless

It is noted that even without the addition of hydrogen peroxide, the ester is superior in odor and color.

EXAMPLE #6 (115-174)

(Preparation of C12–15 Alkyl Benzoate by Other Process)

To 600 grams unfiltered crude ester of Example #5 CR added pre-dissolved 3.0 grams Sodium Chloride and 1.2 grams Sodium Carbonate in 96 grams water. Heated the mixture to 80° C. and acidity of the mixture was <0.1 mg. Added 5.76 grams 35% Hydrogen Peroxide and mixed for an hour at 80° C. Separation was observed upon standing for an hour with interphase of approximately 36 grams. The wash procedure was repeated two more times with predissolved 3.0 grams Sodium Chloride in 96 grams of water and in both cases separation was not sharp, with interphase of approximately 31 and 17 grams was found. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture level was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the: refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	550 grams
Yield % :	91.66
Loss During Washing % :	8.33
Appearance:	Clear liquid
Acid Value:	0.03 mg KOH/g
Water %:	0.01
Refractive Index:	1.48475
Color:	<10 APHA
Saponification Value:	180.92 mg KOH/g
Odor:	Strong Odor

Example #6 is based on the plant-production batch of 10,000 lb. of Example #5CR, where a small amount of approximately one gallon was taken out and filtered in the lab for further study. Before filtration of the one gallon, 600 grams of crude, unfiltered ester was purified by adding hydrogen peroxide to the crude ester at 80° C. to 100° C., then washing with sodium carbonate and sodium sulfate in the presence of the catalyst. The effect of filtration of the catalyst vs. no filtration of the catalyst was compared.

The strong odor of the resulting ester may be explained by the addition of hydrogen peroxide at high temperatures to the anhydrous, unfiltered, crude ester. The stannous oxalate was present in the system to act as a catalyst for oxidation of alcohol to aldehyde when hydrogen peroxide, the source of nascent oxygen, was added.

EXAMPLE #7 (115-176)

(Preparation of C_{12-15} Alkyl Benzoate by Invention Process)

To 600 grams crude ester of Example #5 CR (filtered on Buckner Funnel with Whatman paper #42 in the lab), added pre-dissolved 3.0 grams Sodium Chloride and 1.2 grams Sodium Carbonate in 96 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with interphase of approximately 42 grams. The wash procedure was repeated two more times with pre-dissolved 3.0 grams Sodium Chloride in 96 grams of water and in both cases separation was sharp with interphase of approximately 4 and 0 grams was found. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture level was <0.05%, cooled the mass to 40° C. and added

0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	570 grams
Yield % :	95.00
Loss During Washing % :	5.0
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water %:	0.01
Refractive Index:	1.4850
Color:	<20 APHA
Saponification Value:	182.10 mg KOH/g
Odor:	Practically odorless

In Example #7, the crude ester was filtered to remove the catalyst. As hydrogen peroxide was not added at all, and there was no catalyst in the washing, there is no source of nascent oxygen for an oxidation reaction. Even though there is some free alcohol in the system, the formation of odorous material is practically zero. For this reason, the ester is practically odorless. The extremely low interphases explains the high yield, as interphase is the lost or waste material.

EXAMPLE #8 (118-76)

(Preparation of C_{12-15} Alkyl Benzoate by Invention Process)

To the 340 gram crude ester of Example #5 CR (filtered in the lab on Buckner Funnel with Whatman paper #4.2 added pre-dissolved 8.8 grams Potassium Chloride and 0.5 grams Potassium Carbonate in 88.4 grams water and 1.7 grams 35% Hydrogen Peroxide. Heated the mixture to 80° C. Separation was observed upon standing for an hour with interphase 1.20 grams. The wash procedure was repeated two more times with pre-dissolved 8.8 grams Potassium Chloride in 88.4 grams water and in both cases separation was sharp with interphase of approximately 0.4 and 0.2 grams was found. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture level was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	320 grams
Yield % :	94.41
Loss During Washing % :	5.59
Appearance:	Clear liquid
Acid Value:	0.025 mg KOH/g
Water %:	0.02
Refractive Index:	1.48475
Color:	<5 APHA
Saponification Value:	180.50 mg KOH/g
Odor:	Mild Odor

In Example #8, the alcohol was pretreated with sodium borohydride, the catalyst was filtered, and hydrogen peroxide was added with the neutralization/wash waters, before neutralization of acidity. Salts are used in the second and third washes. The resultant ester has a mild odor.

EXAMPLE #9 (118-78)

(Preparation of C_{12-15} Alkyl Benzoate by Invention Process)

To the 340 gram crude ester of Example #5 CR (filtered in the lab on Buckner Funnel with Whatman paper #42 added pre-dissolved 8.8 grams Potassium chloride and 1.0 grams Potassium Carbonate in 88.4 grams water and 1.7 grams 35% Hydrogen Peroxide. Heated the mixture to 80° C. Separation was observed upon standing for an hour with interphase 13.3 grams. The wash procedure was repeated two more times without Potassium Chloride in 88.4 grams of water and in both cases separation was sharp with no interphase was observed. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	335 grams
Yield % :	98.53
Loss During Washing % :	1.47
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water %:	0.015
Refractive Index:	1.48475
Color:	<5 APHA
Saponification Value:	180.70 mg KOH/g
Odor:	Mild Odor

In Example #9, the same procedure as Example #8 is followed, except that potassium chloride and potassium carbonate salts are not added in the second and third washes. The resultant ester has a mild odor due to the addition of hydrogen peroxide into the system before neutralization of acidity. The yield is high.

EXAMPLE #10 (118-89)

(Preparation of C_{12-15} Alkyl Benzoate by Invention Process)

To the 340 grams crude ester of Example #5 CR (filtered in the lab on Buckner Funnel with Whatman paper #42 added pre-dissolved 8.8 grams Potassium Chloride and 1.7 grams 35% Hydrogen Peroxide in 88.4 grams of water. Heated the mixture to 80° C. and when there was no free Hydrogen Peroxide in the mixture added 1.0 grams Potassium Carbonate and held for one hour at 80° C. Separation was observed upon standing for an hour with interphase 36 grams. The wash procedure was repeated two more times with pre-dissolved Potassium Chloride in 88.4 grams of water and in both cases separation was sharp with interphase of approximately 1 gram was observed. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	330 grams
Yield % :	97.05

-continued

Loss During Washing % :	2.95
Appearance:	Clear liquid
Acid Value:	0.15 mg KOH/g
Water %:	0.01
Refractive Index:	1.48475
Color:	<5 APHA
Saponification Value:	181.05 mg KOH/g
Odor:	Odorless

In Example #10, odorless esters were obtained because the catalyst was filtered, hydrogen peroxide was consumed before addition of potassium carbonate, and the system was aqueous.

EXAMPLE #11 (118-92)

(Preparation of C_{12-15} Alkyl Benzoate by Invention Process)

To the 340 grams crude ester of Example #5 CR (filtered in the lab on Buckner Funnel with Whatman paper #42 added 1.7 grams 35% Hydrogen Peroxide. Heated to 80° C. and mixed for 30 minutes. When there was no free Hydrogen Peroxide, added pre-dissolved 8.8 grams Potassium Chloride and 1.0 grams Potassium Carbonate in 88.4 grams of water. Mixed the mixture at 80° C. for another 30 minutes. Separation was observed upon standing for an hour with interphase of approximately 23 grams. The wash procedure was repeated two more times with predissolved 8.8 grams Potassium Chloride in 88.4 grams of water and in both cases separation wa.45 sharp with interphase of approximately 2 & 1 gram was found. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	325 grams
Yield % :	95.58
Loss During Washing % :	4.42
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water %:	0.015
Refractive Index:	1.4850
Color:	<5 APHA
Saponification Value:	180.75 mg KOH/g
Odor:	Mild Odor

In Example 11, the alcohol was pretreated with sodium: borohydride, the catalyst was filtered, and hydrogen peroxide was added to the ester before the wash; this is not an aqueous system. Some free benzoic acid and alcohol is present in the system. The chances of a reaction between the alcohol, hydrogen peroxide and benzoic acid are favored at that temperature for formation of odorous species. The resultant ester has a mild odor.

EXAMPLE #12 (115-169)

(Preparation of Cetearyl Octanoate by Other Process)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 411.58 grams (1.576 moles) of Cetearyl Alcohol and 238.42 grams (1.655 moles) of Ethylhexanoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 1.95 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over 1 hour. The reaction mixture was then raised to 220° C. in next one hour and held for 5 hours. The distillate (water of reaction) collected was 27.50 grams against theoretical estimates of 29.80 grams. The ester had the acidity of 5.61 mg KOH/g. The reaction mixture was cooled to 100° C. and added 4.0 grams 35% Hydrogen Peroxide. Mixed the reaction mass at 100° C. for an hour and then cooled to 40° C. To the 600 grams crude ester added predissolved 5.0 grams Sodium Carbonate and 7.2 grams Sodium Sulfate in 120 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with 37 grams of interphase was found. The wash procedure repeated two more times with pre-dissolved 7.2 grams Sodium Sulfate in 120 grams of water. In both cases approximately 6 grams of interphase was found upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	520 grams
Yield % :	86.66
Appearance:	Clear liquid
Acid Value:	0.02 mg KOH/g
Water %:	0.02
Color:	<10 APHA
Saponification Value:	140 mg KOH/g
Odor:	Strong Odor

EXAMPLE #13 (118-245)

(Preparation of Cetearyl Octanoate by Process of Invention)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 381.24 grams (1.460 moles) of Cetearyl Alcohol and 216.90 grams (1.50 moles) of 2 Ethylhexanoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 1.80 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over one hour. The reaction mixture was then raised to 220° C. in next hour and held for five hours. The distillate (water of reaction) collected was 24.2 grams against theoretical estimates of 27.12 grams. The ester had the acidity of 3.3 mg KOH/g. The reaction mixture was cooled to 40° C. and filtered on Buckner Funnel with Whatman Paper #4 to remove any residual Stannous Oxalate. To 250 grams filtered crude ester was heated to 80° C. and added predissolved 5.5 grams Sodium Sulfate in 55 grams water and 0.625 grams 35% Hydrogen Peroxide. Mixed the mixture for 30 minutes and when the amount of free Hydrogen Peroxide was 10 ppm added 1.325 grams of Sodium Carbonate. Mixed the mixture for 30 minutes and upon standing a good separation was observed. A minimal amount of interphase of approximately 10 grams was found. The wash procedure was repeated two more times with 5.5 grams Sodium Sulfate pre-dissolved in 55 grams water. In both cases, separation was excellent with less than 1 gram of interphase was found upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 3.0" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and

added 0.1 grams of Diatomaceous Earth filter acids. Mixed the refined eater for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	245 grams
Yield % :	98.00
Appearance:	Clear liquid
Acid Value:	0.02 mg KOH/g
Color:	<20 APHA
Saponification Value:	140 mg KOH/g
Odor:	Practically odorless

EXAMPLE #14 (95-131)

(Preparation of C_{12-15} Alkyl Octanoate by Other Process)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, thermometer, condenser and receiver, added 346.32 grams (1.697 moles) of Neodol 25 (Shell Chemical Company) and 252.248 grams (1.751 moles) of 2 Ethylhexanoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 1.20 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over 1 hour. The reaction mixture was then raised to 220° C. in next hour and held for 3 hours. The distillate (water of reaction) collected was 28.8 grams against theoretical estimates of 31.55 grams. The ester had the acidity of 7.5 mg KOH/g. The reaction mixture was cooled to 100° C. and added 4.0 grams 35% Hydrogen Peroxide. Mixed the reaction mass at 100° C. for an hour and then cooled to 40° C. To the 500 grams crude ester added pre-dissolved 6 grams Sodium Sulfate and 3.0 grams Sodium Carbonate in 100 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with 40 grams of interphase was found. The wash procedure was repeated two more times with pre-dissolved 6.0 grams Sodium Sulfate in 100 grams water. In both cases approximately 8 grams of interphase was found upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	480 grams
Yield % :	92.00
Appearance:	Clear liquid
Color:	<10 APHA
Saponification Value:	165 mg KOH/g
Odor:	Strong odor

EXAMPLE #15 (118-221)

(Preparation of C_{12-15} Alkyl Octanoate by Process of Invention)

In 3000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 1038.96 grams (5.09 moles) of Neodol 25 (Shell Chemical Company) and 757.54 grams (5.26 moles), of 2-Ethylhexanoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 3.6 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over one hour. The reaction mixture was then raised to 220° C. in next hour and held for 3 hours. The distillate (water of reaction) collected was 90.62 grams against theoretical estimates of 94.68 grams. The ester had the acidity of 7.5 mg KOH/g. The reaction mixture was cooled to 40° C. and filtered on Buckner Funnel with Whatman Paper #4 to remove any residual Stannous Oxalate. To the 300 grams filtered crude ester added pre-dissolved 4.5 grams. Sodium Sulfate in 7.5 grams water and 1.25 grams 35% Hydrogen Peroxide. Mixed the mixture at 80° C. for 30 minutes and when the amount of free Hydrogen Peroxide was <10 ppm added 3.0 grams of Sodium Carbonate. Mixed the mixture for 30 minutes and upon standing a separation was observed with approximately 25 grams of interphase was found. The wash procedure was repeated two more times with 4.5 grams Sodium Sulfate pre-dissolved in 75 grams water. In both cases separation was excellent with less than 1 gram interphase found upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	270 grams
Yield % :	96.66
Appearance:	Clear liquid
Acid Value:	0.02 mg KOH/g
Color:	<10 APHA
Saponification Value:	165.8 mg KOH/g
Odor:	odorless

EXAMPLE #16 (105-138)

(Preparation of DPG-Dibenzoate by Other Process)

In 500 ml four neck round bottom flask equipped with glass stirrer, distillation head, thermometer, condenser and receiver added 103.08 grams (0.77 moles) of Dipropylene Glycol and 196.92 grams (1.62 moles) of Benzoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 0.6 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over one hour. The reaction mixture was then raised to 220° C. in next hour and held for six hours. The distillate (water of reaction) collected was 56.5 grams against theoretical estimates of 58.10 grams. The ester had the acidity of 9.8 m KOH/g. The reaction mixture was cooled to 100° C. and added 1.5 grams 35% Hydrogen Peroxide. Mixed the reaction mass at 100° C. for an hour and then cooled to 40° C. To the 264 grams crude ester was added pre-dissolved 10 grams Sodium Chloride and 3.0 grams Sodium Carbonate in 50 grams water. Separation was observed upon standing for an hour with 10 grams of interphase found. The wash procedure was repeated two more times with predissolved 10 grams Sodium Chloride in 50 grams water. In both cases approximately 6 grams of interphase was found upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	220 grams
Yield % :	83.33
Appearance:	Clear liquid
Acid Value:	0.11 mg KOH/g
Water % :	0.02
Color:	<10 APHA
Saponification Value:	310.56 mg KOH/g
Odor:	strong odor

EXAMPLE #17 (118-137)

(Preparation of DPG-Dibenzoate by Process of Invention)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 252.49 grams (1.88 moles) of Dipropylene Glycol and 442.40 grams (3.62 moles) of Benzoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 3.36 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over one hour. The reaction mixture was then raised to 220° C. in next hour and held for six hours. The distillate (water of reaction) collected was 120 grams against theoretical estimates of 130.55 grams. The ester had the acidity of 8.9 mg KOH/g. The reaction mixture was cooled to 40° C. and filtered on Buckner Funnel with Whatman Paper #4 to remove any residual Stannous Oxalate. To the 250 grams filtered crude ester added pre-dissolved 13.37 grams Sodium Chloride in 62.5 grams water and 1.25 grams 35% Hydrogen Peroxide. Mixed the mixture at 80° C. for 30 minutes and when the amount of free Hydrogen Peroxide was <10 ppm added 2.5 grams of Sodium Carbonate. Mixed the mixture for 30 minutes and upon standing a separation was observed with 5 grams of interphase found. The wash procedure was repeated two more times with 13.37 grams Sodium Chloride pre-dissolved in 62.5 grams water. In both cases separation was excellent with less than 1-gram interphase found upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the mixture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	233 grams
Yield % :	93.20
Appearance:	Clear liquid
Acid Value:	0.02 mg KOH/g
Color:	<10 APHA
Saponification Value:	312.58 mg KOH/g
Odor:	odorless

EXAMPLES #18, #19, #20, #21 (REF. Nos. 118-288-A; 118-288-B; 118-288-D; and 118-288-F, REPECTIVELY)

(C12–15 Alkyl Benzoate Esters of Other Process)

These preparations were of plant scale size of 10,000 lb. batches using the processes of Examples #2 and #4. These are based on other processes and were used for comparative purposes against the products of the invention processes.

EXAMPLES #22 and #22-C (118-288-A-NP and 118-288-C-NP)

(C_{12-15} Alkyl Benzoate Esters of Invention Process)

These preparations were large plant scale of 10,000-lb. size using the procedures of Examples #5 and #5CR. These are based on the invention processes.

EXAMPLES #23 and #24

(C12–15 Alkyl Octanoate Esters of Other Processes)

These preparations were of 10,000 lb. batch sizes using the other processes of Example #14.

EXAMPLE #25 (118-225)

(Preparation of C_{12-15} Alkyl Octanoate by Process of Invention)

To the 300 grams filtered crude ester from Example #15 added pre-dissolved 4.5 grams Sodium Sulfate and 3.0 grams Sodium Carbonate in 75 grams water and 1.25 grams 35% Hydrogen Peroxide. Mixed the mixture for 30 minutes and upon standing a separation was observed with approximately 30 grams of Interphase. The wash procedure was repeated two more times with 4.5 grams Sodium Sulfate-predissolved in 75 grams water. In both cases separation was observed with less than 4 grams Interphase upon'standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	265 grams
Yield % :	88.33
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water %:	0.03
Color:	<10 APHA
Saponification Value:	165.8 mg KOH/g
Odor:	odorless

EXAMPLE #26 (118-227)

(Preparation of C_{12-15} Alkyl Octanoate by Process of Invention)

To the 300 grams filtered crude ester from Example #15 added pre-dissolved 4.5 grams Sodium Sulfate and 3.0 grams Sodium Carbonate in 75 grams water. Mixed the mixture for 30 minutes and upon standing a separation was observed with approximately 20 grams of Interphase. The wash procedure was repeated two more times with 4.5 grams Sodium Sulfate pre-dissolved in 75 grams water. In both cases separation was observed with less than 2 grams Interphase upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	275 grams
Yield % :	91.66
Appearance:	Clear liquid
Acid Value:	0.02 mg KOH/g
Water %:	0.03
Color:	<20 APHA
Saponification Value:	165.8 mg KOH/g
Odor:	practically odorless

EXAMPLE #27 (118-301-A-OP)

(Preparation of Cetearyl Octanoate by Other Process)

In 2000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 628.7 grams (2.45 moles) of Cetearyl Alcohol and 371.3 grams (2.57 moles) of Ethylhexanoic Acid. The temperature was raised to 80° C. with good flow of nitrogen. At 80° C. added 3.00 grams of Stannous Oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over one hour. The reaction mixture was then raised to 220° C. in next hour and held for five hours. The distillate (water of reaction) collected was 43.8 grams against theoretical estimates of 46.4 grams. The ester had the acidity of 6.4 mg KOH/g. The reaction mixture was cooled to 100° C. and added 7.5 grams 35% Hydrogen Peroxide. Mixed the reaction mass at 100° C. for an hour and then cooled to 40° C. To the 930 grams crude ester added pre-dissolved 12.0 grams Sodium Sulfate and 10.0 grams Sodium Carbonate in 200 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with 52 grams of Interphase. The wash procedure repeated two more times with pre-dissolved 12.0 grams Sodium Sulfate in 200 grams of water. In both cases approximately 10 grams of Interphase was found upon standing. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter acids. Mixed the refined eater for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	821 grams
Yield % :	88.28
Appearance:	Clear liquid
Acid Value:	0.03 mg KOH/g
Water %:	0.01
Color:	<10 APHA
Saponification Value:	141 mg KOH/g
Odor:	strong odor

EXAMPLE #28 (118-301-B-NP)

(Cetearyl Octanoate)

This preparation was of 10,000-lb. batch size using the process of this invention as shown in Example #13.

EXAMPLE #29 (118-310)

(Preparation of C_{12-15} Alkyl Benzoate per U.S. Pat. No. 4,322,545 to Scala)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 368.1 grams (1.805 moles) of Neodol 25. (Shell Chemical Company), 225.54 grams (1.850 moles) of Benzoic Acid, and 12 grams of Methane Sulfonic Acid. The temperature was raised to 170° C. with good flow of nitrogen in next two hours and held for 4 hours so at 170° C. until acid value <10 mg. KOH/g. The distillate (water of reaction) collected was 30 grams against theoretical estimates of 33.2 grams. The reaction mixture was cooled to 100° C. and added 2 grams of 35% Hydrogen Peroxide. The resulting light colored ester was cooled to 40° C. To the 560 grams crude ester added pre-dissolved 2.8 grams Sodium Chloride and 5.6 grams Sodium Carbonate in 90 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with a big amount of Interphase of approximately 46 grams. The wash procedure was repeated two more times with predissolved 2.85 grams Sodium Chloride in 90 grams of water. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass 10 to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	500 grams
Yield % :	89.28
Loss During Washing % :	10.72
Appearance:	Clear liquid
Acid Value:	0.01 mg KOH/g
Water % :	0.02
Refractive Index:	1.4835
Color:	70 APHA
Saponification Value:	171.6 mg KOH/g
Odor:	Strong odor

The foregoing Ex. #29 follows Example Nos. 1, 2 and 3 of U.S. Pat. No. 4,322,545 to Scala, except that use of hydrogen peroxide is not taught in the '545 Patent. Hydrogen peroxide has been added in Ex. #29 at 100° C. to demonstrate that addition of hydrogen peroxide yields an ester of strong odor, and yet has higher color, too.

EXAMPLE #30 (118-311)

(Preparation of C_{12-15} Alkyl Benzoate per U.S. Pat. No. 4,322,545 to Scala)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 368.1 grams (1.805 moles) of Neodol 25 (Shell Chemical Company), 225.54 grams (1.850 moles) of Benzoic Acid, and 12 grams of Methane Sulfonic Acid. The temperature was raised to 170° C. with good flow of nitrogen in next two hours and held for 4 hours at 170° C. until acid value <10 mg. KOH/g. The distillate (water of reaction) collected was 30 grams against theoretical estimates of 33.2 grams. The reaction mixture was cooled to 40° C. To the 560 grams light-yellow colored, crude ester was added pre-dissolved 2.8 grams Sodium Chloride and 5.6 grams Sodium Carbonate in 90 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with a big amount of Interphase of approximately 49 grams. The wash procedure was repeated two more times with predissolved 2.85 grams Sodium Chloride in 90 grams of water. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of

Diatomaceous-Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	498 grams
Yield % :	88.93
Loss During Washing % :	11.07
Appearance:	Light-yellowish color clear liquid
Acid Value:	0.01 mg KOH/g
Water % :	0.03
Refractive Index:	1.4835
Color:	100 APHA
Saponification Value:	171.4 mg KOH/g
Odor:	Strong odor

The foregoing Ex. #30 follows Example Nos. 1, 2 and 3 of U.S. Pat. No. 4,322,545 to Scala. Hydrogen peroxide is not added. The resulting product has even worse color and odor than Ex. #29 above, where hydrogen peroxide was added.

EXAMPLE #31 (118-312)

(Preparation of Octyldodecyl Benzoate as per U.S. Pat. No. 4,791,097 to Walele et al.)

In 1000 ml four neck round bottom flask equipped with glass stirrer, distillation head, condenser, thermometer and receiver, added 426 grams (1.43 moles) of STANDAMUL G from Henkel Co. (Octyldodecanol). Pretreated with 30 mgms of Sodium Borohydride and 172.8 gms (1.41 moles) of Benzoic Acid. The temperature was raised to 80° C. with good flow of Nitrogen. At 80° C., added 0.9 grams of Stannous oxalate and continued to heat to 200° C. maintaining a good flow of nitrogen over 1 hour. The reaction mixture was then raised to 255° C. in next 2 hours and held at 255° C. for one hour. The distillate (water of reaction) collected was 22 grams against theoretical estimates of 25.4 grams. The ester had the acidity of <10 mg. KOH/g. The reaction mixture was cooled to 60° C. To the 575 grams crude ester, added 3.0 grams of Sodium Chloride, 5.43 grams Sodium Carbonate, and 3.0 grams 35% Hydrogen Peroxide predissolved in 90 grams water. Heated the mixture to 80° C. Separation was observed upon standing for an hour with a big amount of Interphase of approximately 60 grams. The wash procedure was repeated two more times with predissolved 3.0 grams Sodium Chloride in 90 grams of water. The washed aqueous ester was then heated to 120° C. with a vacuum of 30" Hg to remove any residual moisture and organic volatiles. When the moisture was <0.05%, cooled the mass to 40° C. and added 0.1 grams of Diatomaceous Earth filter aids. Mixed the refined ester for 30 minutes and filtered on Buckner Funnel with Whatman Paper #42.

The following physical and chemical properties were observed:

Yield:	505 grams
Yield % :	87.82
Loss During Washing % :	12.18
Appearance:	Clear liquid
Acid Value:	0.02 mg KOH/g
Water % :	0.025
Color:	40 APHA

-continued

Saponification Value:	131 mg KOH/g
Odor:	Strong odor

The foregoing Ex. #31 follows Example No. 1 of U.S. Pat. No. 4,791,097 to Walele et al. Hydrogen peroxide is added simultaneously during and at the time of neutralization. The resulting ester has strong odor and high color. In contrast, the invention process uses hydrogen peroxide, if at all, after the neutralization, and not before or at the time of neutralization.

Personal Care Product Formulations Containing Benzoic Acid Esters

To further demonstrate the superiority of the esters of the invention, a series of formulations was prepared comparing the odor characteristics of various personal care products formulated with the compositions of the invention, and with other esters which are commonly used in such types of products. The products specifically included a moisturizing body lotion, an emollient cleansing lotion, and a makeup remover gel. These are considered to be representative of formulations wherein the esters of the invention find application.

Properties of and Uses for Benzoic Acid Ester Compositions

The formulations containing the esters of this invention do not need a higher level of fragrance to mask their presence due to their zero odor or none/negligible odor. Such formulations are desired where unfragranced products are made on demand by consumers. This is also a trend on the market place for hypoallergenic formulations.

EXAMPLE #32

An unfragranced, moisturizing body lotion prepared using the compositions of the present invention has outstanding attributes in that the benzoate esters of this invention, when utilized as a emollient, impart practically no odor of their own to the moisturizing body lotion. Additionally, the body lotion, when applied to the skin, produces a pleasant sensation, and conditions the skin. A representative moisturizing body lotion formulation was prepared, utilizing the following ingredients in the proportions indicated:

TABLE IF

Light Moisturizing Lotion for Table I

Ingredients (INCI)	% BY WT.
A. Water	85.0
Carbomer (Ultrez 10)[1]	0.6
Propylene Glycol	3.0
Sodium C12–15 Pareth-8 Carboxylate (SURFINE WLG-2 CONC.)[2]	0.3
B. Emollient Ester	10.0
C. Triethanolamine, 99%	0.6
D. Propylene Glycol, Diazolidinyl Urea, Methylparaben and Propylparaben (Germaben 11)[3]	0.5

[1]B F Goodrich Company, Cleveland, OH 44131
[2]Finetex, Inc., Elmwood Park, NJ 07407
[3]ISP, Wayne, NJ 07470

Procedure

1. Disperse carbomer in water. Heat to 65° C.–70° C. Add propylene glycol and SURFINE WLG-2 CONC.
2. Weigh (B) items. Heat to 65° C.–70° C.
3. Add (B) to (A) with stirring.
4. Add triethanolamine with vigorous stirring.
5. Cool to 45° C. Add preservative. Continue stirring to room temperature.

EXAMPLE #33

In this Example, another moisturizing body lotion was prepared, fragranced at two levels. The formulation was as follows:

TABLE IIF

Light Moisturizing Lotions for Table II-A and II-B

	Ingredients (INCI)	% by wt. Fragrance Level A	B
A.	Water	84.90	84.80
	Carbomer (Ultrez 10)[1]	0.60	0.60
	Sodium C12–15 Pareth-8 Carboxylate (SURFINE WLG-2 CONC.)[2]	0.30	0.30
B.	Emollient Ester	10.00	10.00
C.	Triethanolamine, 99%	0.60	0.60
D.	Propylene Glycol, Diazolidinyl Urea, Methylparaben and Propylparaben (Germaben II)[3]	0.50	0.50
	Fragrance Bouquet 39465[4] (1:500 dilute an aliquat in Propylene Glycol)	0.10	0.20

[1]B F Goodrich Company, Cleveland, OH 44131
[2]Finetex, Inc., Elmwood Park, NJ 07407
[3]ISP, Wayne, NJ 07470
[4]Intarome Fragrance Corp., Norwood, NJ 07646

Procedure

1. Disperse carbomer in water. Heat to 65° C.–70° C. Add propylene glycol and SURFINE WLG-2 CONC.
2. Weigh (B) items. Heat to 65° C.–70° C.
3. Add (B) to (A) with stirring.
4. Add triethanolamine with vigorous stirring.
5. Cool to 45° C. Add preservative and fragrance. Continue stirring to room temperature.

EXAMPLE #34

An example of a representative emollient cleansing lotion is as follows:

TABLE IV-F

Emollient Cleansing Lotion for Table IV

	Ingredients (INCI)	% by wt.
A.	Water	80.9
	Disodium Oleamide MIPA Sulfosuccinate (FIZUL MD-318C)[1]	1.0
	Glycerine	3.0
	Carbomer (Carbopol ETD 2001 Resin)[2]	0.2
	Tetrasodium EDTA	0.1
B.	Emollient Ester	7.5
	Stearic Acid, XXX	3.0
	Glyceryl Stearate, SE	2.0
C.	Water	1.0
	Triethanolamine, 99%	0.8

TABLE IV-F-continued

Emollient Cleansing Lotion for Table IV

	Ingredients (INCI)	% by wt.
D.	Propylene Glycol, Diazolidinyl Urea, Methylparaben and Propylparaben (Germaben II)[3]	0.5

[1]Finetex, Inc. Elmwood Park, NJ 07407
[2]B F Goodrich Company, Cleveland, OH 44131
[3]ISP, Wayne, NJ 07470

Procedure

1. Disperse carbomer into water. Add balance of (A) ingredients and heat to 70° C.–75° C.
2. Mix (B) ingredients together and heat to 70° C.–75° C. Add (B) to (A) with mixing.
3. Combine (C) ingredients, then add to the mixture of (A) & (B).
4. Begin to cool with mixing. At 40° C., add (D). Continue cooling to 30° C. Package in a suitable container.

EXAMPLE #35

An example of make-up remover gel containing an emollient ester is as follows:

TABLE V-F

Make-up Remover Gel for Table V

	Ingredients (INCI)	% BY WT.
A.	Emollient Ester	12.0
	Sodium Laureth-13 carboxylate (SURFINE WLL)[1]	26.0
	Oleth-2	7.0
	Alpha - Tocopherol Acetate	0.2
	Propylene Glycol	4.0
	Sorbitol, 70%	7.0
B.	Water	43.6
C.	DMDM - Hydantoin	0.2

[1]Finetex Inc. Elmwood Park, NJ 07407

Procedure

Combine components of (A) and mix while heating to 75° C. Heat water to 75° C.–80° C. and add to (A). Continue mixing as it cools. At 55° C., add DMDM—Hydantoin and continue mixing until 45° C. and package in a suitable container.

EXAMPLE #36

Odor Panel Test Results

The odor/fragrance panel tests conducted were subjective in nature—nine individuals were requested to evaluate the odor using a scale of 1 to signify the "least" odor, and 10 for the "most" odor. The results are set forth in Tables I, IIA and IIB, IIIA through IIID, IV and V, from which it will be seen that the esters of this invention are superior in having significantly less odor than esters produced by conventional processes.

The average score is shown to be less than 2 for the esters of this invention versus an average score of greater than 7 for the esters of the other processes. The gap between the two ratings is very extensive, demonstrating the superiority of the esters of this invention in terms of odor.

The importance of this lack of odor is especially critical in fragrance applications, where it is noted that all formulations have a minimum fragrance level (MFL) at which the formulation no longer has an inherent odor. To establish a detectable level of fragrance, a slight increase in fragrance level must be achieved to overcome the inherent odor of the formulation. That is to say, to overcome odors, it is necessary to use more fragrance.

Table I shows the odor panel results for the unfragranced series, namely, on the moisturizing body lotion formulated as in Table I-F (Example #29 above), where no fragrance is added to the formulation. The odor results of the unfragranced series shows the superiority of the esters of the present invention vs. the esters manufactured by prior art processes. The odor of the control formulation (water instead of ester) is 1. The esters of this invention give formulations that are distinctly close in fragrance/odor of the blank control formulation containing water instead of the emollient ester, other ingredients remaining common to all formulations. The formulations AA, BB, CC, and DD containing the esters of the present invention are odorless. The esters of the other processes A, B, C, and D, are easily identified in their respective formulations by their respective typical/characteristic odors.

Tables II-A and II-B show the odor panel results for the fragranced series, namely, on the moisturizing body lotion formulated as in Table II-F (Example #30 above). The fragranced series of tests was conducted to demonstrate that the esters of the invention allow the reduced use of fragrance as compared to the conventional esters of other processes.

Referring to Tables II-A and II-B, the fragranced formulations series, the fragrance used was at two levels: level A was at 0.10% and level B was at 0.20%. In this series, each ester of the invention and the equivalent esters of the other process were compared at both levels of fragrance.

The esters of this invention show that a lower level of fragrance is adequate to produce a perfumed product. The products of the other process need higher levels of fragrance to produce an equal strength perfumed product. This also indicates that any odor-masking requirement of the esters produced by other processes consumed or demanded a higher level dose of fragrance in over-coming their respective characteristic odors. This further indicates that the MFL (Minimum Fragrance Level) for esters of this invention is lower than the MFL of esters of the other processes. The fragrance of the formulations containing esters of this invention showed lower ratings, thus demonstrating superiority to the esters of other processes at both levels of fragrance.

The same phenomenon is expected in other personal care product formulations which advantageously use esters of this invention.

The results of odor or perfume/fragrance reduction panel tests are shown in Tables I, II-A and II-B for cosmetics/personal care formulations described above in Examples # 29-32. By the Odor AS IS Basis is meant odor panel comparisons done on the neat (as is) products of this invention vs. the products of the other processes.

EXAMPLE 37

Results of Odor Panel Tests for FINESOLV TN, FINESTER EH-25, FINESTER CST-8, and FINSOLV PG-22.

A further evaluation of odor was conducted for compositions in accordance with the invention, and for esters produced in accordance with known processes. More specifically, esters described in the above Examples, produced in accordance with the process of the invention and by known processes, were compared by again requesting 9 individuals to evaluate odor using a scale of 1 to equal "least" and 10 to equal "most". The results are set forth in Tables III-A through III-D, from which it is clear that the esters of the invention are far superior to products including FINESOLV TN, FINESTER EH-25, FINESTER CST-8, and FINSOLV PG-22.

TABLE III compares odor, color and yields for each of the ester prepared in Examples 1 through 17, 25–27, and 29–30. It will be seen that esters prepared by the process of the invention are superior in odor, color and yield to esters prepared by known processes.

In conclusion, the esters of the invention are surprisingly found to be virtually lacking in detectable odor, superior in color, and produced in greater yields.

It will be understood that the embodiments described herein are merely exemplary and that a person skilled in the art may make many variations and modifications without departing from the spirit and scope of the invention. For example, the invention is not intended to be strictly limited to the named reactants and catalysts, recited pH ranges, reaction temperatures, reaction conversion, or other parameters. Rather, the invention as claimed extends to many possible variations not specifically detailed. All such variations and modifications are intended to be included in the scope of the invention as described herein.

TABLE I

		Odor Panel Results on Moisturizing Body Lotion (Unfragranced Series) See Formulation Table I-F							
		A	B	C	D	AA	BB	CC	DD
		Other Process				New Invention Process			
	Control	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate
Emollient Esters of:									
Other Process	None	+	+	+	+	—	—	—	—
New Process	None	—	—	—	—	+	+	+	+
Example #	Water	4	16	14	12	6	17	15	13
Odor Panel Results									

1 = Best
10 = Worst

TABLE I-continued

Odor Panel Results on Moisturizing Body Lotion (Unfragranced Series)
See Formulation Table I-F

		A	B	C	D	AA	BB	CC	DD
		Other Process				New Invention Process			
	Control	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate
Panel Ratings:									
1.	1	8	9	9	8	2	2	2	2
2.	1	9	7	10	8	3	2	1	2
3.	1	10	8	8	9	2	1	3	1
4.	1	7	8	9	8	3	2	1	2
5.	1	7	7	8	10	1	1	2	1
6.	1	8	7	7	8	2	1	1	3
7.	1	9	8	9	9	1	1	2	2
8.	1	8	8	8	8	1	1	1	1
9.	1	7	9	8	10	2	2	1	2
Total Score =	9.0	73	71	76	78	17	13	14	16
Average Score =	1.00	8.11	7.88	8.44	8.66	1.88	1.44	1.55	1.77

TABLE II-A

Odor Panel Results on Moisturizing Body Lotion
(fragranced Series: Level A @ 0.10% of Fragance)
See Formulation Table II-F

		A	B	C	D	AA	BB	CC	DD
		Other Process				New Invention Process			
	Control	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate
Emollient Esters of:									
Other Process	None	+	+	+	+	—	—	—	—
New Process	None	—	—	—	—	+	+	+	+
Example #	Water	4	16	14	12	6	17	15	13
Odor Panel Results									
1 = Best 10 = Worst Panel Ratings:									
1.	1	7	8	8	7	2	2	2	1
2.	1	7	7	8	7	1	2	1	2
3.	1	7	8	9	8	1	1	1	1
4.	1	8	8	8	9	2	1	1	1
5.	1	8	7	7	7	1	2	2	2
6.	1	7	6	8	8	1	1	1	1
7.	1	6	6	8	7	1	1	1	2
8.	1	7	7	7	9	1	2	2	1
9.	1	8	7	9	8	1	2	1	1
Total Score =	9	65	64	72	70	11	14	12	12
Average Score =	1.0	7.22	7.11	8.00	7.77	1.22	1.55	1.33	1.33

TABLE II-B

Odor Panel Results on Moisturizing Body Lotion (Fragranced Series: Level B @ 0.2% of Fragance) See Formulation Table II-F

		A	B	C	D	AA	BB	CC	DD
		Other Process				New Invention Process			
	Control	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate
Emollient Esters of:									
Other Process	None	+	+	+	+	—	—	—	—
New Process	None	—	—	—	—	+	+	+	+
Example #	Water	4	16	14	12	6	17	15	13
Odor Panel Results									
1 = Best 10 = Worst Panel Ratings:									
1.	1	6	7	7	6	1	2	1	1
2.	1	7	6	7	6	2	1	1	2
3.	1	6	7	8	7	1	1	2	1
4.	1	6	7	7	8	1	1	1	1
5.	1	5	6	6	6	2	2	1	1
6.	1	5	6	7	7	1	1	1	2
7.	1	6	7	7	7	1	1	1	1
8.	1	6	7	8	8	1	2	2	1
9.	1	6	7	7	7	1	1	1	1
Total Score =	9	53	54	64	62	11	12	11	11
Average Score =	1.0	5.88	6.0	7.11	6.88	1.22	1.33	1.22	1.22

TABLE III

Comparison Of Odor, Color, and % Yield

Process[1]	Example #	Odor	APHA[2] Color	% Yields
NP	1. (115-178)	Odorless	15	97.75
OP	2. (112-51)	Strong Odor	5	95.00
NP	3. (121-90)	Odorless	20	96.25
OP	4. (112-141)	Mild Odor	5	96.00
OP	5. (Motherbatch) (115-72)	Odorless	20	93.33
OP	6. (115-174)	Strong Odor	10	91.66
	7. (115-176)	Odorless	20	95.00
	8. (118-76)	Mild Odor	5	94.41
NP	9. (118-78)	Mild Odor	5	98.53
NP	10. (118-89)	Odorless	5	97.05
NP	11. (118-92)	Mild Odor	5	95.58
OP	12. (115-169)	Strong Odor	10	86.66
NP	13. (118-245)	Odorless	20	98.00
OP	14. (95-131)	Strong Odor	10	92.00
NP	15. (118-221)	Odorless	10	96.66
OP	16. (105-138)	Strong Odor	10	83.33
NP	17. (118-137)	Odorless	10	93.20

TABLE III-continued

Comparison Of Odor, Color, and % Yield

Process[1]	Example #	Odor	APHA[2] Color	% Yields
NP	25. (118-225)	Odorless	10	88.33
NP	26. (118-227)	Odorless	20	91.66
OP	27. (118-301A)	Strong Odor	10	88.28
OP	29. (118-310)	Strong Odor	70	89.28
OP	30. (118-311)	Strong Odor	100	88.93
OP	31. (118-312)	Strong Odor	40	87.82

[1]NP = New Process, OP = Other Process

[2]APHA SCALE = American Public Health Association ASTM D-1209

TABLE III-A

Odor Panel Results on C12–15 Alkyl Benzoate (FINSOLV TN)[1] Other Process vs. Invention Process

Panel	1	2	3	4	5	6	7	8	9
Old Process Series									
Example #18 Lot A (Ref. #118-288-A)	9	9	5	10	9	9	9	10	10
Example #19	7	9	8	10	10	10	4	9	10

TABLE III-A-continued

Odor Panel Results on C12–15 Alkyl Benzoate (FINSOLV TN)[1]
Other Process vs. Invention Process

Panel	1	2	3	4	5	6	7	8	9
Lot B (Ref. #118-288-B)									
Example #2	10	8	10	9	10	9	8	8	7
Lot C (Ref. #112-51)									
Example #20	6	7	4	6	10	5	5	4	5
Lot D (Ref. #118-288-D)									
Example #4	6	6	9	6	8	7	7	3	5
Lot E (Ref. #112-141)									
Example #21	6	6	7	7	9	6	6	4	5
Lot F (Ref. #118-288-F)									
New Process Series									
Example #22	1	1	4	2	2	1	4	2	1
Lot A (Ref. #118-288-A-NP)									
Example #6	1	1	2	1	1	1	3	2	1
Lot B (Ref. #115-174)									
Example #22-C	2	1	3	2	2	1	2	1	1
Lot C (Ref. #118-288-C-NP)									
Example #1	1	2	2	1	1	2	1	1	1
Lot D (Ref. #115-178)									
Rating:	10 Worst 1 Best								
Results:									
Average of Panelists and Products	Other Process 7.30 New Process 1.70								

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TABLE III-B

Odor Panel Results on C12–15 Alkyl Octanoate (FINESTER EH-25)[1]
Other Process vs. New Invention Process

Panel	1	2	3	4	5	6	7	8	9
Old Process Series									
Example #14	8	9	8	8	10	7	8	8	8
Lot A (Ref. #118-300-A)									
Example #23	8	10	6	9	8	8	7	9	7
Lot B (Ref. #118-300-B)									
Example #24	9	8	7	7	7	7	9	8	9
Lot C (Ref. #118-300-C)									
New Process Series									
Example #15	2	1	1	2	2	2	2	2	1
Lot A (Ref. 118-221)									
Example #25	2	2	3	1	1	2	1	1	1
Lot B (Ref. #118-225)									
Example #26	2	1	1	1	2	2	1	2	2
Lot C (Ref. #118-227)									
Rating:	10 Worst 1 Best								
Results:									
Average of Panelists and Products	Other Process 8.03 New Process 1.59								

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TABLE III-C

Odor Panel Results on C12–15 Cetearyl Octanoate (FINESTER CST-8)[1]
Other Process vs. New Invention Process

Panel	1	2	3	4	5	6	7	8	9
Old Process Series									
Example #12	8	9	10	9	10	9	8	10	8
Lot A (Ref. #115-169)									

TABLE III-C-continued

Odor Panel Results on C12–15 Cetearyl Octanoate (FINESTER CST-8)[1]
Other Process vs. New Invention Process

Panel	1	2	3	4	5	6	7	8	9
Example #27 Lot B (Ref. #118-301) New Process Series	10	10	8	8	7	7	10	8	9
Example #13 Lot. A (Ref. #118-245)	1	2	3	2	1	3	2	1	2
Example #28 Lot B (Ref. #118-301-B)	2	2	1	1	3	1	2	2	1
Rating:	10 Worst 1 Best								
Results:									
Average of Panelists and Products	Other Process 7.78								
	New Process 1.77								

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TABLE III-D

Odor Panel Results on Dipropylene Glycol Dibenzoate (FINSOLV PG-22)[1]
Other Process vs. New Invention Process

Panel	1	2	3	4	5	6	7	8	9
Old Process									
Example #16 (Ref. #105-138) New Process	9	8	10	10	7	8	9	8	8
Example #17 (Ref. #118-137)	2	1	2	1	2	3	1	3	2
Rating:	10 Worst 1 Best								
Results:									
Average of Panelists and Products	Other Process 7.56								
	New Process 1.89								

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TABLE IV

Odor Panel Results on Emollient Cleansing Lotion
See Formulation Table III

		A	B	C	D	AA	BB	CC	DD
		Other Process				New Invention Process			
	Control	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate
Emollient Esters of:									
Other Process	None	+	+	+	+	—	—	—	—
New Process	None	—	—	—	—	+	+	+	+
Example #	Water	4	16	14	12	6	17	15	13
Odor Panel Results									
1 = Best 10 = Worst Panel Ratings:									
1.	1	9	8	8	10	3	2	4	4
2.	1	10	9	9	9	4	2	3	4
3.	1	9	10	8	9	2	4	3	3
4.	1	8	9	9	10	3	4	2	3
5.	1	9	8	10	8	4	3	4	4
6.	1	8	8	9	9	3	2	4	2

TABLE IV-continued

	Odor Panel Results on Emollient Cleansing Lotion See Formulation Table III								
		A	B	C	D	AA	BB	CC	DD
		Other Process				New Invention Process			
	Control	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate
7.	1	8	9	9	10	4	3	2	3
8.	1	9	8	9	9	2	4	3	2
9.	1	8	10	9	10	2	4	3	4
Total Score =	9	78	79	80	84	27	30	28	29
Average Score =	1.0	8.66	8.77	8.88	9.33	3.0	3.33	3.11	3.22

TABLE V

	Odor Panel Results on Make-up Remover Gel See Formulation Table V-F								
		A	B	C	D	AA	BB	CC	DD
		Other Process				New Invention Process			
	Control	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate	C12–15 Alkyl Benzoate	Dipropylene Glycol Dibenzoate	C12–15 Alkyl Octanoate	Cetearyl Octanoate
Emollient Esters of:									
Other Process	None	+	+	+	+	—	—	—	—
New Process	None	—	—	—	—	+	+	+	+
Example #	Water	4	16	14	12	6	17	15	13
Odor Panel Results									
1 = Best 10 = Worst Panel Ratings:									
1.	1	8	9	8	9	2	2	3	3
2.	1	9	8	9	8	3	4	2	3
3.	1	8	9	8	9	1	3	3	3
4.	1	10	9	9	8	1	2	2	2
5.	1	9	8	10	8	2	2	2	3
6.	1	8	9	9	9	1	2	2	2
7.	1	8	8	8	9	3	3	2	2
8.	1	9	8	8	8	1	2	2	2
9.	1	8	8	9	9	1	2	3	2
Total Score =	9	82	76	78	77	15	19	21	22
Average Score =	1.0	9.11	8.44	8.66	8.55	1.66	2.11	2.33	2.44

We claim:

1. A method of reducing or eliminating odor in an ester composition comprising a crude ester and an esterification catalyst comprising the step of removing said catalyst from the crude ester and then adding alkali to neutralize acidity.

2. In a process for preparing odorless, colorless esters from an esterification reaction mixture obtained by reacting an acid and an alcohol in the presence of an effective amount of a catalyst, which comprises adding alkali to the esterification reaction mixture and washing the ester, the improvement which comprises removing said catalyst from said reaction mixture prior to addition of alkali and which further comprises contacting the wet, crude ester with a bleaching agent, after neutralization with said alkali is completed.

3. The process of claim 2 wherein said odorless esters are benzoate esters, octanoate esters, aliphatic emollient esters, or glycol dibenzoate esters, wherein said acid is selected from the group consisting of benzoic acid, ethylhexanoic acid, and linear or branched carboxylic acids with 4 to 22 carbon atoms, and wherein said alcohol has from 3 to 22 carbon atoms.

4. In a process for preparing reduced-odor benzoate esters from an esterification reaction mixture obtained by reacting benzoic acid with an alcohol in the presence of an effective amount of a catalyst, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization.

5. The process of claim 5 wherein said catalyst comprises an organometallic compound or metal oxide compound.

6. The process of claim 4 wherein said catalyst is stannous oxalate or zinc oxide.

7. The process of claim 4 wherein said catalyst is removed by filtration.

8. The process of claim 4 wherein said neutralization step, the filtered, crude ester is neutral washed with amounts of alkali at least stoichiometric to the acidity of the crude ester.

9. The process of claim 4 wherein said alkali comprises an alkali metal carbonate or alkali metal hydroxide.

10. In a process for preparing reduced-odor benzoate esters from an esterification reaction mixture obtained by reacting benzoic acid with an alcohol in the presence of an effective amount of a catalyst, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization, and wherein after said neutralization is completed, contacting the wet, crude ester with a bleaching agent.

11. The process of claim 4 wherein said bleaching agent is hydrogen peroxide.

12. In a process for preparing reduced-odor benzoate esters from an esterification reaction mixture obtained by reacting benzoic acid with an alcohol in the presence of an effective amount of a catalyst, which comprises the steps of:

beating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization, and wherein said wet, crude ester is contacted with a bleaching agent in a first or subsequent washing step, after neutralization is complete.

13. The process of claim 4 wherein said alcohol comprises from 3 to 22 carbon atoms.

14. The process of claim 4 wherein said alcohol comprises 12 to 15 carbon atoms.

15. The process of claim 4 wherein said crude ester has an acidity of no more than 10 mg KOH/g.

16. The process of claim 4 further comprising pretreating said alcohol with sodium borohydride before reacting with benzoic acid and before contacting with said catalyst.

17. The process of claim 4 wherein said neutralization wash further comprises at least one salt selected from the group consisting of sodium chloride, sodium sulfite, potassium chloride and potassium sulfate.

18. The process of claim 4 further comprising the step of cooling said reaction mixture after said reaction is substantially complete and before said neutralization step.

19. The process of claim 4 comprising the step of further washing the resulting crude ester after said neutralization and washing step.

20. The process of claim 19 wherein at least one salt selected from the group consisting of sodium chloride, sodium sulfate, potassium chloride, and potassium sulfate is added in at least one of said washing steps.

21. The process of claim 4 wherein distillate is collected until esterification is substantially complete.

22. The process of claim 4 wherein said process is a batch process.

23. The process of claim 4 wherein said process is a continuous process.

24. The process of claim 23 wherein said process is conducted in a continuous extractor.

25. In a process for preparing reduced-odor octanoate esters from an esterification reaction mixture obtained by reacting ethylhexanoic acid with an alcohol in the presence of an effective amount of a catalyst, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization.

26. The process of claim 25 wherein said alcohol comprises from 3 to 22 carbon atoms.

27. The process of claim 25 wherein said alcohol comprises 12 to 15 carbon atoms.

28. The process of claim 25 wherein said catalyst is stannous oxalate or zinc oxide.

29. In a process for preparing reduced-odor octanoate esters from an esterification reaction mixture obtained by reacting ethylhexanoic acid with an alcohol in the presence of an effective amount of a catalyst, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization, and wherein after said neutralization is completed, contacting the wet, crude ester with a bleaching agent.

30. In a process for preparing reduced odor aliphatic, emollient esters from an esterification reaction mixture obtained by reacting a carboxylic acid with an alcohol in the presence of an effective amount of a catalyst, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization.

31. The process of claim 30 wherein said alcohol comprises from 3 to 22 carbon atoms and wherein said carboxylic acid comprises linear or branched carboxylic acids with 4 to 22 carbon atoms.

32. The process of claim 30 wherein said alcohol comprises 12 to 15 carbon atoms.

33. The process of claim 30 wherein said catalyst is stannous oxalate or zinc oxide.

34. In a process for preparing reduced odor aliphatic, emollient esters from an esterification reaction mixture

obtained by reacting a carboxylic acid with an alcohol in the presence of an effective amount of a catalyst, wherein said alcohol comprises from 3 to 22 carbon atoms and wherein said carboxylic acid comprises linear or branched carboxylic acids with 4 to 22 carbon atoms, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization, and wherein after said neutralization is completed, contacting the wet, crude ester with a bleaching agent.

35. In a process for preparing reduced odor glycol dibenozate ester from an esterification reaction mixture obtained by reacting a glycol with benzoic acid in the presence of an effective amount of a catalyst, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization.

36. The process of claim **35** wherein said glycol comprises from 3 to 12 carbon atoms.

37. The process of claim **35** wherein said glycol comprises 6 to 12 carbon atoms.

38. The process of claim **35** wherein said glycol is dipropylene glycol.

39. The process of claim **35** wherein said catalyst is stannous oxalate or zinc oxide.

40. In a process for preparing reduced odor glycol dibenozate esters from an esterification reaction mixture obtained by reacting a glycol with benzoic acid in the presence of an effective amount of a catalyst, which comprises the steps of:

heating said reaction mixture;

collecting distillate comprising the water of reaction;

neutralizing and washing the acidity of said reaction mixture with at least one alkali;

drying said ester; and

filtering the refined ester product;

the improvement comprising removing said catalyst from said reaction mixture after the reaction is complete, and before neutralization, and wherein after said neutralization is completed, contacting the wet, crude ester with a bleaching agent.

41. The process of claim **4** wherein said alcohol is Neodol 25.

42. The process of claim **25** wherein said alcohol is Neodol 25.

43. The process of claim **30** wherein said alcohol is Neodol 25.

* * * * *

EXHIBIT - 3

US005998120A

United States Patent [19]

Connelly et al.

[11] Patent Number: 5,998,120

[45] Date of Patent: Dec. 7, 1999

[54] **PROCESS FOR MAKING A DIRECT DISPERSION OF A PHOTOGRAPHICALLY USEFUL MATERIAL**

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[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[21] Appl. No.: **09/000,597**

[22] Filed: **Dec. 30, 1997**

[51] **Int. Cl.**[6] **G03C 1/047**

[52] **U.S. Cl.** **430/539**; 430/642; 430/546; 430/631; 430/354

[58] **Field of Search** 430/449, 546, 430/642, 539, 631; 530/354

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Attorney, Agent, or Firm—Andrew J. Anderson

[57] **ABSTRACT**

A process for making a direct dispersion of a photographically useful material is discloses comprising: mixing (i) an aqueous phase comprising a gelatin solution and (ii) a liquid organic phase comprising a photographically useful material under conditions of high shear or turbulence to form a fine dispersion of the organic phase having an average particle size of less than 0.5 micron dispersed in the aqueous phase; wherein the gelatin solution comprises a mixture of a first gelatin having an isoelectric point pH of less than or equal to 5.2 and a second gelatin having an isoelectric point pH of greater than or equal to 6.0. In accordance with the invention, the use of blends of a first gelatin having an pI of less than or equal to 5.2, such as a conventional lime processed gelatin, and a second gelatin having an pI of greater than or equal to 6.0, such as an acid processed gelatin, in a direct photographic dispersion yields a substantial reduction in viscosity in comparison to the use of the first gelatin alone, which reduction is greater than would be expected by just using blends of the first gelatin with another relatively low pI gelatin having an equivalent inherent viscosity as the second gelatin. In accordance with preferred embodiments of the invention, relatively low levels of APO gelatin may be used partially replacing LPO gelatin in a dispersion formulation to obtain significant viscosity reduction while minimizing adverse effects which may be associated with the use of higher levels of acid processed gelatin.

24 Claims, No Drawings

luminescent dyes, antifoggants, stabilizers, light absorbing and scattering materials, coating aids, plasticizers, lubricants, antistats and matting agents are described, for example, in Sections VI–IX. Layers and layer arrangements, color negative and color positive features, scan facilitating features, supports, exposure and processing can be found in Sections XI–XX.

In practicing the present invention, a hydrophobic PUM is melted by heat or dissolved in an organic solvent prior to homogenization. Materials that have a relatively low melting point, e.g. below 90° C., can be dispersed without the use of organic solvents. The molten mixture of the PUM with or without the permanent solvent is termed the liquid organic (or oil) phase.

Where the liquid organic phase includes an organic solvent, it is preferred to use high-boiling or permanent organic solvents. High boiling solvents have a boiling point sufficiently high, generally above 150° C. at atmospheric pressure, such that they are not evaporated under normal dispersion making and photographic layer coating procedures. Non-limiting examples of high boiling organic solvents that may be used include the following.

S-1	Dibutyl phthalate
S-2	Tritolyl phosphate
S-3	N,N-Diethyldodecanamide
S-4	Tris(2-ethylhexyl)phosphate
S-5	Octyl oleate monoepoxide
S-6	2,5-Di-t-pentylphenol
S-7	Acetyl tributyl citrate
S-8	1,4-Cyclohexylenedimethylene bis(2-ethylhexanoate)
S-9	Bis(2-ethylhexyl)phthalate
S-10	2-phenylethyl benzoate
S-11	Dibutyl sebacate
S-12	N,N-Dibutyldodecanamide
S-13	Oleylalcohol
S-14	2-(2-Butoxyethoxy)ethyl acetate

It is an advantage of the process of the invention that auxiliary solvents are not essential for forming fine dispersions, and it is preferred that direct dispersions are prepared wherein essentially no volatile or water-miscible organic solvent is present in the organic phase. In accordance with particularly preferred embodiments, such direct dispersions may be prepared where the organic phase comprises at least 16 weight percent, more preferably at least 17 weight percent, and most preferably at least 18 weight percent, of the dispersion even in the absence of auxiliary solvents. Inclusion of such solvents in photographic elements, however, may be desirable in certain situations to achieve photographic properties not directly related to the dispersion making process, and their presence will not interfere with the process of the invention. Most useful auxiliary solvents are water immiscible, volatile solvents, and solvents with limited water solubility which are not completely water miscible. Non-limiting examples of these include the following.

A-1	Ethyl acetate
A-2	Cyclohexanone
A-3	4-Methyl-2-pentanol
A-4	Triethyl phosphate
A-5	Methylene chloride
A-6	Tetrahydrofuran

The aqueous phase of the dispersions of the invention comprises a mixture of at least two distinct gelatins, the first of which has an pI of less than or equal to 5.2, preferably from 4.8–5.1, and most preferably about 4.9–5.0, and the second of which has an pI of greater than or equal to 6.0, preferably from 6.0–9.5, more preferably from 6.0–8.0, and most preferably about 6.0–7.5. The first gelatin preferably comprises a lime processed ossein (LPO) gelatin which exhibits a solution viscosity of at least 4.0 cP, more preferably at least about 7.0 cP and most preferably at least about 12.0 cP, wherein the solution viscosity of the gelatin is measured as a 10 wt'% aqueous solution at a temperature of 45° C. and a pH of 5.7, as the invention is particularly useful for decreasing dispersion viscosity while maintaining the physical advantages provided by the use of higher viscosity gelatins. The most preferred LPO gelatins for use in accordance with the invention are typically distinguished from lower viscosity gelatins in that they contain greater than 40% by weight of molecules having a molecular weight greater than 150,000 daltons. Lime processed gelatins may contain a significant calcium ion concentration (e.g., typically about 3000 ppm), or may be deionized to result in much lower calcium concentrations. Dispersions obtained in accordance with the invention are particularly useful wherein the first gelatin comprises a decalcified lime processed ossein gelatin, as such gelatins typically result in relatively higher dispersion viscosities. The second gelatin preferably comprises an acid processed gelatin which exhibits a solution viscosity of less than or equal to about 150%, and more preferably less than or equal to about 100%, of the first gelatin solution viscosity, wherein the solution viscosity of each gelatin is measured as 10 wt % aqueous solutions at a temperature of 45° C. and a pH of 5.7, in order to optimize the dispersion viscosity reducing advantages in accordance with the invention. The second gelatin is most preferably an acid processed ossein (APO) gelatin having an pI of from 6.0–7.5. The total amount of gelatin in the dispersions of the invention may be typically used at levels up to 30 wt % based on the total amount of the aqueous phase, more preferably from 3–25 wt %, and most preferably 5–20 wt %.

The weight ratio of the first gelatin to the second gelatin in the dispersions of the invention is preferably from about 1:3 to 20:1, more preferably from about 1:1 to 10:1, and most preferably from about 1:1 to 3:1. Dispersions prepared in accordance with the invention employing a second gelatin having a substantially higher pI value than the first gelatin have been found to exhibit lower viscosities than are obtained by mixing an equivalent amount of a second gelatin having an equivalent solution viscosity as measured in a 10 wt % aqueous solution but which does not have a distinct pI value as required by the invention. This allows relatively low dispersion viscosities to be obtained while using only a fraction of a higher pI value second gelatin, thus avoiding undesirable effects which may be associated with the use of high levels of such high pI gelatins. In many cases, dispersions prepared using only a minor fraction of the relatively high pI value second gelatin in accordance with the invention exhibit viscosities which are comparable to, or even lower than, those obtained for dispersions employing an equivalent amount of only the high pI value gelatin, while substantially retaining the benefits supplied by a major fraction of the relatively low pI value first gelatin. In accordance with such embodiments of the invention, the relatively high pI value second gelatin thus preferably comprises less than 50 weight percent of the total gelatin, most preferably from about 10–45 weight percent of the total gelatin.

It is preferable to include surfactants in the aqueous solution. The surfactant is preferably an anionic or nonionic surfactant, including fluorosurfactants. For purposes of this invention, a surfactant is a surface active material which is capable of depressing the surface tension of distilled water by at least 20 dynes/cm at its critical micelle concentration at 25° C. Anionic surface active agents preferably have the $—SO_3^-$ or $—OSO_3^-$ moiety. Preferred anionic surface active agents include naphthalenesulfonic acids, sulfosuc-

EXHIBIT - 6

Finetex®

TECHNICAL DATA SHEET

FINSOLV® TPP*

INCI NAME: *C12-15 ALKYL BENZOATE (and) DIPROPYLENE GLYCOL DIBENZOATE (and) PPG-15 STEARYL ETHER BENZOATE*

U.S. Patent No. 4,791,097

INTRODUCTION

FINSOLV® TPP is a proprietary blend of three unique benzoate esters, which exhibit performance synergy in several personal care product areas.

First, **FINSOLV TPP** is an exceptional solvent for sunscreen actives. **FINSOLV TPP** will solubilize 30% benzophone-3 and avobenzone (Parsol 1789) compared to 16% for **FINSOLV® TN***. This allows for higher active levels and improved product stability with less chance of recrystalization.

Second, **FINSOLV TPP** exhibits exceptional tactile and performance improvements over the individual materials. The C12-15 alkyl benzoate moiety exhibits a soft, smooth, non-greasy rub in while the dipropylene glycol dibenzoate adds an occlusive property and the PPG-15 stearyl ether benzoate helps in coupling the three esters. This unique blend of emolliency and occlusiveness combine to produce a moisturizer with superior tactile and performance properties.

Finally, **FINSOLV TPP** is soluble in a wider range of materials than its individual components. This in combination with its sunscreen solubility and moisturization attributes makes **FINSOLV TPP** a truly unique and functional emollient.

TOXICOLOGY

Toxicology data on the individual components is available upon request.

Finetex®

FINSOLV® TPP

TYPICAL PROPERTIES (Not intended as specifications)

APPEARANCE	Clear, almost colorless to pale yellow liquid
ODOR	Very mild
POUR POINT	-13°C (approx.)
FLASH POINT	>300°F
SPECIFIC GRAVITY @ 25°C	0.945
REFRACTIVE INDEX @ 20°C	1.490
SURFACE TENSION @ 15°C, (Du Nuoy)	34 dynes/cm.
INTERFACIAL TENSION IN WATER @ 15°C	9 dynes/cm.
SPREADING COEFFICIENT @ 15°C	29 dynes/cm.
VISCOSITY, Brookfield @ 70°F, RV #1 Spindle, 100 RPM	55cps
COLOR, APHA	20
SAPONIFICATION VALUE, (mg KOH/g)	195

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FINSOLV® TPP

SOLUBILITY

ACETONE	Soluble
BEESWAX*	Soluble
CASTOR OIL	Soluble
ETHANOL	Soluble
ISOPROPANOL	Soluble
ISOPROPYL MYRISTATE	Soluble
ISOPROPYL PALMITATE	Soluble
LANOLIN	Soluble
PARAFFIN WAX*	Soluble
VOLATILE SILICONES	Soluble
VEGETABLE OIL	Soluble

*Soluble Hot

APPLICATIONS

The multifunctional properties of **FINSOLV TPP** will find applications in the following personal care areas:

- *Skin Care* as a moisturizer, emollient and skin conditioning agent, which imparts a light, dry and non-oily, feel to the skin.
- *Sun Care* for improved solubilization of active materials and enhanced tactile properties.
- *Antiperspirant/Deodorants* to reduce the white residue left on the skin from antiperspirant salts. In addition, the high refractive index of **FINSOLV TPP** makes it suitable for use in clear products.

Rev. 4/00
*Patent Pending

Visit us at www.finetexinc.com

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EXHIBIT - 7

Finetex®

TECHNICAL DATA SHEET

FINSOLV® PG-22*

INCI NAME: *DIPROPYLENE GLYCOL DIBENZOATE*

INTRODUCTION

FINSOLV® PG-22 is an efficient skin conditioning agent functioning as both a humectant and emollient. Acting on the upper layers of the skin to enhance moisturization, leaving the skin soft, smooth and supple, reducing flaking and improving the skin's overall appearance. In addition, due to the dibenzoate portion of the molecule, **FINSOLV PG-22** is an excellent solvent and solubilizer, aiding in the formulation of clear products.

TYPICAL PROPERTIES (Not intended as specifications)

APPEARANCE	Clear, almost colorless to pale yellow liquid
ODOR	Very mild
POUR POINT, °C	Approx. -20
FLASH POINT, °F	>200
SPECIFIC GRAVITY @ 25°C	1.120
REFRACTIVE INDEX @ 20°C	1.5240
VISCOSITY, cps. @ 20°C	165
COLOR, APHA	20
SAPONIFICATION VALUE, (mg KOH/g)	305
MOISTURE, %	<0.25

Finetex®

FINSOLV® PG-22

SOLUBILITY

WATER	Insoluble
PROPYLENE GLYCOL	Insoluble
GLYCERIN	Insoluble
ETHANOL	Soluble
CYCLOMETHICONE	Insoluble
DIMETHICONE	Insoluble
MINERAL OIL	Insoluble
VEGETABLE OIL	Soluble
FINSOLV TN*	Soluble

APPLICATIONS

Due to its unique tactile properties, solubility in water/alcohol mixtures and refractive index, **FINSOLV PG-22** is an excellent candidate for use in clear, personal care products such as antiperspirants and deodorants.

In addition, **FINSOLV PG-22** is an excellent additive in both leave-in and rinse off hair care formulations adding humectancy and moisture to the hair as well as considerable shine.

Rev. 4/00
*Patent Pending

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EXHIBIT - 8

Finetex®

TECHNICAL DATA SHEET

FINSOLV® EB*

INCI NAME: *ETHYLHEXYL BENZOATE*

INTRODUCTION

FINSOLV® EB is a branched emollient ester, which provides excellent moisturization to the skin, leaving a soft, smooth, yet exceptionally light afterfeel.

CAS Registry Number : *5444-75-7*
EINECS Number : *226-641-8*

TYPICAL PROPERTIES (Not intended as specifications)

APPEARANCE	Clear almost colorless liquid
COLOR, APHA	20
ODOR	Mild
FLASH POINT	>200°F
POUR POINT	Less then –17°C
SPECIFIC GRAVITY @ 20°C	0.9615
REFRACTIVE INDEX @ 20°C	1.492
SURFACE TENSION @ 15°C	35.1 dynes/cm
VISCOSITY, Brookfield @ 70°F, RV #1 Spindle, 100 RPM	25 cps
SAPONIFICATION VALUE, (mg KOH/g)	235

TOXICOLOGY

Ocular Irritation (Rabbits)	Practically Non-irritating
Primary Skin Irritation	1.55 (Not a Primary Dermal Irritant)

Finetex®

FINSOLV® EB

SOLUBILITY

FINSOLV® ESTERS (all)	Soluble
ALIPHATIC ESTERS	Soluble
CYCLOMETHICONE	Soluble
DIMETHICONE	Insoluble
MINERAL OIL	Soluble
PROPYLENE GLYCOL	Insoluble
GLYCERIN	Insoluble
WATER	Insoluble

APPLICATIONS

FINSOLV EB is a valuable additive to all types of Personal Care products due to its light, dry feel and quick absorbency. **FINSOLV EB** can effectively be used in conjunction with volatile silicones to enhance moisturization and emolliency without oiliness. In addition, the high solvency properties make it an excellent additive to Sunscreen Preparations.

Rev. 6/21/02

* Patent Pending

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EXHIBIT - 10

PRESENTATION OF DERMATEST GmbH

STAFF MEMBERS

The Company Dermatest was founded in 1978 and since then it is situated in Münster, Westfalen. The managing director is Dr. med W.Voss. After his medical study at the universitiy of Münster he worked at the Fachklinik Hornheide (Münster) to get his degree in dermatology, venerology and allergology. From 1978-1983 he worked in an office first together with another specialist for dermatology, since 1983 on his own. He took his doctors degree upon the vitalhistology of pigmented skin tumors in 1974. Because of his great interest in science he started to do medical and cosmetical research work beside his work as a practitioner. At the moment there are another three specialists of dermatology and venerology in his company, one of them additional is specialised in allergology, futhermore two secretaries and one consulting-room assistant with qualification for cosmetician are employed.

SERVICES

For 25 years we do testings of skin functions and clinical controlled in–use tests for cosmetic and pharmaceutic products, for example:

- **Patch tests**
- **Repetitive patch tests**
- **Photo-patch tests**
- **in-use tests for dermatological, ophtalmological and dental products to test their tolerability and efficacy**
- **market research about acceptance and contentment of the tested products**
- **Laserprofilometric tests acc. to DIN**
- **Light protection factor measurements acc. to DIN and COLIPA**
- **UVA protection factor measurements acc. to the Australian Standard**
- **Skin moisture determination with corneometer**
- **TEWL measurements with evaporimeter**
- **Sebumetry**
- **Skin elasticity determination with the cutometer**

Because of our close contact to patients in our daily work as practitioners we are able to recruit test persons for very special questions. E.g. products which should be labelled especially for sensitive skin are tested on persons with atopic skin in the eczema free intervall.

We also cooperate with other medical disciplines. In case of testing eye make-up we consult ophtalmologists, in case of testing bleeching ointments for the teeth we cooperate with

3.2. Broadspectrum evaluation acc. to Diffey

In this method a single index called the critical wavelength is defined as the wavelength where the integral of the absorbance curve reaches 90 percent of the integral from 290 to 400 nm. Diffey suggests that this critical wavelength can be useful to describe the broadness of the protection offered by a sunscreen product as an adjunct to the SPF. If the critical wavelength remains under 325 nm (low UVA protection) there is no evaluation. Critical wavelengths between 325- 335 nm are labelled on the product with one star, critical wavelengths between 335- 350nm with two stars, critical wavelengths between 350- 370 nm with three stars and values higher than 370 nm with four stars (high UV protection).

3.3. Boots Star Rating System

In this method the UVA protection of a product is related to its UVB protection. This method is commonly used in Great Britain. The ratio of the integral of the absorbance curves between 320-400 nm (UVA) and between 290-320 nm (UVB) is calculated. High protection is correlated with a quotient near 1.

3.4. Light protection acc. to the Australian Standard

The percentage transmittance of UVA radiation is measured between wavelengths of 320 and 360. The Australian Standard is fulfilled, when maximal 10 % of the UVA light are transmitted.

We do these measurement with the **Labsphere UV1000 Transmittance Analyser.**

This presentation was just meant to give you a short overview about our technical equipment and our company work. It is far from completeness but I hope you got a first impression and I could raise your interest.